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(54) COMPONENT GRADIENT COMPOSITE OF ORGANIC POLYMER AND METAL OXIDE AND ITS PRODUCTION

(57)Abstract:
PURPOSE: To obtain the subject component gradient composite favorable in terms of effectively manifesting such characteristics as to be seen in the case of high content of the metal oxide as a component, less apt to develop cracks, and having such good moldability as not to cause only the surface layer thereof when heated or after change in its properties with the lapse of time.
CONSTITUTION: This composite essentially comprises an organic polymer component and a metal oxide component A, having such component gradient structure that the content of the metal oxide component A in the composite lies continuously changed from the surface of the composite toward the depth, being 5-100wt.% and 0-50wt.% in the regions presenting higher content levels including the maximum and lower levels including the minimum, respectively, and the content ratio in these regions stands at ≥1.5. This composite is obtained by the following process: a homogeneous solution containing the organic polymer and a metal alkoxide is applied on an organic polymer or inorganic base material and held in an aerial atmosphere containing water and/or a polymerization catalyst for the metal alkoxide followed by drying and then heat treatment.

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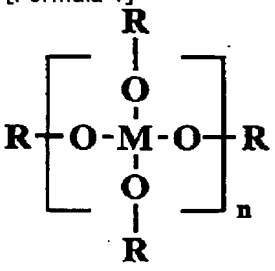
* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] It is the complex of the organic macromolecule and metallic oxide containing an organic macromolecule component and at least two sorts of components of a metallic-oxide component (A). It has the component inclination structure where the content in the inside of the complex of a metallic-oxide component (A) changes in the depth direction from the front face of complex continuously. And component inclination complex of the organic macromolecule and metallic oxide which are characterized by being 0 - 50 % of the weight, and the ratio of the content of a high place and a low place being 1.5 or more in 5 - 100 % of the weight, and the lowest location in the location where the content concerned is the highest.
[Claim 2] Component inclination complex of the organic macromolecule and metallic oxide according to claim 1 with which a metallic-oxide component (A) is characterized by being obtained under existence of an organic macromolecule component according to a metal alkoxide, or its hydrolysis and polycondensation of a low condensate.
[Claim 3] Claim 1 to which a metallic-oxide component (A) is characterized by existing exceeding the average content in the whole complex in at least one front face of complex, and component inclination complex of the organic macromolecule of two publications, and a metallic oxide.
[Claim 4] Claim 1 to which a metallic-oxide component (A) is characterized by existing by the ratio below the average content in the whole complex in at least one front face of complex, and component inclination complex of the organic macromolecule of two publications, and a metallic oxide.
[Claim 5] Component inclination complex of the organic macromolecule and metallic oxide according to claim 1 to 4 which are characterized by the thickness (d1) from which the content of a metallic-oxide component (A) is changing continuously being larger than the thickness (d2) which shows the highest content of a metallic-oxide component (A) in the depth direction of complex.
[Claim 6] Component inclination complex of the organic macromolecule of any one publication of claim 1-5 and metallic oxide with which magnitude of the metallic oxide in complex is characterized by being the pitch diameter of 0.01-5 micrometers.
[Claim 7] Component inclination complex of the organic macromolecule and metallic oxide according to claim 6 with which magnitude of the metallic oxide in complex is characterized by being the pitch diameter of 0.01-0.5 micrometers.
[Claim 8] Component inclination complex of the organic macromolecule of any one publication of patent claim 2-7 and metallic oxide which are characterized by a metal alkoxide or its condensate being what is expressed with a general formula 1.
[Formula 1]



(Among a formula, in M, CmH2m+1 and m express the integer of 1-4, and, as for n, a silicon atom and R express the integer of 1-10.)
[Claim 9] Component inclination complex of the organic macromolecule of any one publication of claim 1-8 and metallic oxide which are characterized by an organic macromolecule component being thermosetting resin.
[Claim 10] Component inclination complex of the organic macromolecule of any one publication of patent claim 1-8 and metallic oxide which are characterized by an organic macromolecule component being thermoplastics.
[Claim 11] The manufacture approach of the component inclination complex of the organic macromolecule and metallic oxide which are characterized by performing desiccation and heat treatment after holding what applied the homogeneity solution which consists of an organic macromolecule, metal alkoxides, and those common solvents on the organic macromolecule or the inorganic base material under the ambient atmosphere which included the polymerization catalyst of water and/or a metal alkoxide in air.

[Claim 12] The manufacturing method of the component component inclination complex of the organic macromolecule and metallic oxide according to claim 11 which are characterized by including an organic solvent in the air ambient atmosphere in which the polymerization catalyst of water and/or a metal alkoxide was included further.

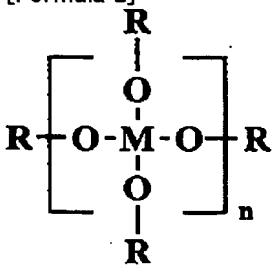
[Claim 13] The manufacturing method of the component component inclination complex of the organic macromolecule and metallic oxide according to claim 12 which are characterized by being that in which the organic solvent contained in an ambient atmosphere differs from the organic solvent used for preparation of a homogeneity solution.

[Claim 14] The manufacturing method of the component component inclination complex of the organic macromolecule of any one publication of claim 11–13 and metallic oxide which are characterized by including the polymerization catalyst of a metal alkoxide further in the homogeneity solution which consists of an organic macromolecule, metal alkoxides, and those common solvents.

[Claim 15] The manufacture approach of the component inclination complex of the organic macromolecule of any one publication of claim 11–14 and metallic oxide with which the polymerization catalyst of the metal alkoxide contained in an air ambient atmosphere or a homogeneity solution is characterized by being congener or an alkali of a different kind.

[Claim 16] The manufacturing method of the component component inclination complex of the organic macromolecule of any one publication of claim 11–15 and metallic oxide which are characterized by being the silicon alkoxide a metal alkoxide is indicated to be by the general formula 1, or its low condensate.

[Formula 2]



(Among a formula, in M, CmH2m+1 and m express the integer of 1–4, and, as for n, a silicon atom and R express the integer of 1–10.)

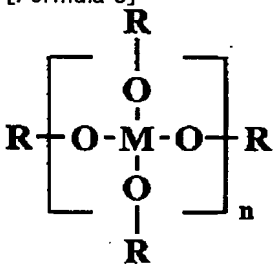
[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the component inclination complex and its manufacturing method of the organic macromolecule and metallic oxide which are characterized by having the field where the content of a metallic oxide differs in inclination in the thickness direction of complex in the complex of the metallic oxide and the organic macromolecule which are obtained by hydrolysis and the polycondensation reaction of a metal alkoxide.

[0002]
[Description of the Prior Art] In order to reform the engine performance of an organic macromolecule, the resin which the approach of former versatility is examined, blends two or more organic macromolecules, and has a new property is prepared, or preparing the Plastic solid which compound-izes with reinforcing materials of a different kind, and has the target property etc. is performed widely.
[0003] For example, by blend compound-ization of organic giant molecules, it considers as homogeneous complex by approaches, such as melting mixing, and reforming of the organic giant molecule according to the purpose of use has been made by devising and blending mixed conditions etc. so that it may have the specific decentralized structure which looks for the organic giant molecule in which compatibility is shown, and includes microfacies isolation construction for the organic giant molecule which is immiscible nature.
[0004] On the other hand, physical-properties reforming by making an organic macromolecule mix and distribute reinforcement is also examined broadly. Specifically mixing powdered inorganic materials, such as a fibrous material organic [, such as an aramid fiber, pulp, a glass fiber, and a carbon fiber,] or inorganic, a calcium carbonate, a silica, and an alumina, etc. with an organic macromolecule is performed widely.
[0005] Compound-ization especially by mixing with an inorganic material has been widely considered as an easy high performance reforming means from the ability of the thermal resistance which was excellent in the inorganic material, or a mechanical property to be employed efficiently. However, in the case of an inorganic material, it is common to be compound-ized for the purpose of it not being easy to control a distributed condition micro, and obtaining the most homogeneous chiefly possible bulk composite material from the difference in an essential property with the organic polymeric materials in points, such as the thermal infusibility, chemical insolubility, high specific gravity, and a surface characteristic.
[0006] That is, in order to raise the reforming effectiveness, it has a smaller configuration, and a wettability good thing with a matrix macromolecule is chosen as an inorganic material for reinforcement, and it has become an important factor in compound-izing that only the specified quantity distributes them to homogeneity as much as possible. However, even in this case, an inorganic material has the problem which homogeneity distribution becomes difficult and becomes energy and what is high also in cost, so that it becomes particle-like.
[0007] Therefore, in order to obtain the composite of the organic material of the high performance which consists of an organic material and a particle-like inorganic material and by which it was homogeneous in micro and the decentralized structure was controlled, and an inorganic material, it is completely difficult and a new technique needs to be developed of the above approaches of only mixing a particle-like inorganic material with an organic macromolecule.
[0008] this invention persons have performed development research of the composite of effective new organic material and non-equipments to such a purpose. As the example, there are micro hybrid composites of the metallic oxide and the organic giant molecule which are obtained for example, from a metal alkoxide.
[0009] It is the composite material of the organic material which the wettability of the metallic-oxide particle of MIKURONO-DA [from NANOO-DA -] - is good in an organic macromolecule by performing hydrolysis and the polycondensation of a metal alkoxide by in-situ in an organic macromolecule matrix, and this complex is compound [distribution and]-ized by homogeneity, and has the properties which were very excellent including a mechanical property, and non-equipments.
[0010] However, if the metallic-oxide component rate in this complex is enlarged too much, good composite will no longer be obtained according to the difference of the essential property of the organic macromolecule and metallic oxide which are compound-ized. That is, in what has high metallic-oxide content, that it is easy to produce a crack, become, become weak, a moldability worsens, and deformation of curvature, distortion, etc. is produced. On the other hand, by the thing of a minute amount, desired composite nature is no longer obtained for metallic-oxide content.
[0011]

[Problem(s) to be Solved by the Invention] The technical problem which this invention tends to solve is obtaining the good complex which may discover effectively the property to the high content field of a metallic oxide, and is to offer the component inclination complex and its manufacturing method of the organic macromolecule and metallic oxide which have a good moldability which a crack cannot more specifically produce easily and exfoliation of only a surface side produces neither by heating nor aging.
[0012]
[Means for Solving the Problem] In the complex which consists of an organic macromolecule and a metallic oxide, this invention person etc. tackles research wholeheartedly so that he may get the complex which has the property which was excellent in the wide range presentation field, and he comes to complete this research.
[0013] Namely, this invention is the complex of the organic macromolecule and metallic oxide containing an organic macromolecule component and at least two sorts of components of a metallic-oxide component (A). The content in the inside of the complex of a metallic-oxide component (A) changes in the depth direction from the front face of complex continuously. It has component inclination structure and is the component inclination complex of the organic macromolecule and metallic oxide which are 0 - 50 % of the weight, and are characterized by the ratio of the content of a high place and a low place being 1.5 or more in 5 - 100 % of the weight, and the lowest location in the location where the content concerned is the highest.
[0014] The component inclination complex of the organic macromolecule of this invention and a metallic oxide is component inclination complex of the organic macromolecule and metallic oxide with which the metallic-oxide component (A) is characterized by being obtained under existence of an organic macromolecule component according to a metal alkoxide, or its hydrolysis and polycondensation of a low condensate in detail.
[0015] Moreover, the component inclination complex of the organic macromolecule of this invention and a metallic oxide is detailed, and it is characterized by the metallic-oxide component (A) existing in at least one front face of complex exceeding the average content in the whole complex.
[0016] Furthermore, the component inclination complex of the organic macromolecule of this invention and a metallic oxide is component inclination complex of the organic macromolecule and metallic oxide with which a metallic-oxide component (A) is characterized by existing by the ratio below the average content in the whole complex in at least one front face of complex.
[0017] Moreover, the component inclination complex of the organic macromolecule of this invention and a metallic oxide is component inclination complex of the organic macromolecule and metallic oxide which are characterized by the thickness (d1) from which the content of a metallic-oxide component (A) is changing continuously being larger than the thickness (d2) which shows the highest content of a metallic-oxide component (A) in the depth direction of complex.
[0018] Furthermore, the component inclination complex of the organic macromolecule of this invention and a metallic oxide contains the component inclination complex of the component inclination complex of the organic macromolecule and metallic oxide with which magnitude of the metallic oxide in complex is characterized by being the pitch diameter of 0.01-5 micrometers, and the organic macromolecule and metallic oxide with which magnitude of the metallic oxide in complex is characterized by being the pitch diameter of 0.01-0.5 micrometers.
[0019] Moreover, the component inclination complex of the organic macromolecule of this invention and a metallic oxide is component inclination complex of the organic macromolecule and metallic oxide which are characterized by being what the metallic-oxide component is obtained under existence of an organic macromolecule component according to a metal alkoxide, or its hydrolysis and polycondensation of a low condensate, and the metal alkoxide or its condensate is especially expressed with a general formula 1 to.
[0020] (General formula 1)
[Formula 3]



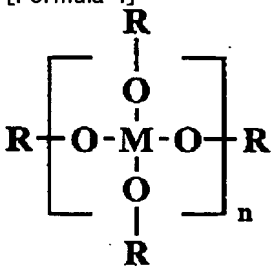
(Among a formula, in M, CmH2m+1 and m express the integer of 1-4, and, as for n, a silicon atom and R express the integer of 1-10.)
[0021] Moreover, the component inclination complex of the organic macromolecule of this invention and a metallic oxide is component inclination complex of the organic macromolecule and metallic oxide which are characterized by an organic macromolecule component being thermosetting resin.
[0022] Moreover, the component inclination complex of the organic macromolecule of this invention and a metallic oxide is component inclination complex of the organic macromolecule and metallic oxide which are characterized by an organic macromolecule component being thermoplastics.
[0023] This invention includes the manufacture approach of the component inclination complex of the organic macromolecule and the metallic oxide which are characterized by performing desiccation and heat treatment, after holding what applied the homogeneity solution which consists of an organic macromolecule, metal alkoxides, those

common solvents, and/or a polymerization catalyst of a metal alkoxide on the organic macromolecule or the inorganic base material under the ambient atmosphere which included the polymerization catalyst and/or organic solvent of water and/or a metal alkoxide in air.

[0024] The manufacture approach of the component inclination complex of the organic macromolecule of this invention and a metallic oxide is a manufacturing method of the component component inclination complex of the organic macromolecule and the metallic oxide which are characterized by being the silicon alkoxide with which the metallic-oxide component distributes to homogeneity, and is obtained in an organic macromolecule component under existence of an organic macromolecule component according to a metal alkoxide, or its hydrolysis and polycondensation of a low condensate, and especially a metal alkoxide is indicated to be by the general formula 1, or its low condensate.

[0025] (General formula 1)

[Formula 4]



(Among a formula, in M, CmH2m+1 and m express the integer of 1-4, and, as for n, a silicon atom and R express the integer of 1-10.)

[0026] Moreover, especially the manufacture approach of the component inclination complex of the organic macromolecule of this invention and a metallic oxide includes the manufacture approach of the component inclination complex of the organic macromolecule and metallic oxide which are characterized by using congener or an alkali of a different kind as a polymerization catalyst of the metal alkoxide contained in an ambient atmosphere and/or a homogeneity solution.

[0027] That is, this invention is forming the component inclination structure where exist by the concentration from which the metallic-oxide component to contain differs in the interior of complex in the complex of the organic macromolecule per sort [at least], the organic macromolecule containing a metallic oxide, and a metallic oxide, and metallic-oxide constituent concentration changes in the depth direction from the front face of complex continuously, and [0028]. And the metallic-oxide constituent concentration in complex is 0 - 50 % of the weight in 5 - 100 % of the weight, and the lowest place in the highest place, And it is a thing about the component inclination complex of the organic macromolecule and metallic oxide which are characterized by the ratio of the content of a high place and a low place being 1.5 or more. It centers on the component inclination complex of the organic macromolecule and metallic oxide which consist of a metallic oxide especially obtained under organic macromolecule existence by carrying out the polycondensation of a metal alkoxide or its low condensate, and an organic macromolecule.

[0029] In the component inclination complex of the organic macromolecule and a metallic oxide concerned, that whose metallic-oxide component is below the average metallic-oxide concentration of complex is included in at least one front face of complex in the thing in which the metallic-oxide component exists exceeding the average metallic-oxide concentration of complex, or at least one front face. Moreover, the component inclination complex of the organic macromolecule and a metallic oxide concerned contains what has the larger thickness which has a metallic-oxide concentration inclination than the thickness which has the highest content of a metallic oxide in the depth direction.

[0030] Moreover, the component inclination complex of the organic macromolecule and a metallic oxide concerned contains that whose magnitude of the metallic oxide contained in complex is the pitch diameter of 0.01 micrometers - 5 micrometers. Moreover, the gestalt is a paint film, yarn, a film, and a spherical thing, and also the component inclination complex of the organic macromolecule and a metallic oxide concerned contains what is the Plastic solid of various configurations, such as a block.

[0031] In this invention, while a metallic oxide maintains homogeneity into an organic macromolecule except the depth direction, it is based on having the field which is changing in the depth direction continuously. Therefore, it differs in what has the field where metallic-oxide concentration differs nonsequetially by only irregular condensation and phase separation, the thing which has the homogeneity paint film which has the fixed metallic-oxide content formed of paint on the front face of a base material.

[0032] As an organic macromolecule which can be used for this invention, according to the polycondensation of the metal alkoxide under organic macromolecule existence Although not limited especially, just possible [building the complex of a homogeneous organic macromolecule and a homogeneous metallic oxide] specifically For example, phenol resin, an epoxy resin, acrylic resin, alkyd resin, Thermosetting resin, such as melamine resin and a urea-resin, nylon, polyester, It is possible to use thermoplastics, such as acrylic resin, polybutadiene, rubber system resin like SBS, etc., and an epoxy resin, acrylic resin, alkyd resin, and melamine resin are especially desirable also in thermosetting resin.

[0033] What is the organic macromolecule which dissolves in the homogeneity solution which consists of its

condensate, them, a solvent, etc. in the viewpoint from the ease on manufacture, or is swollen, or its precursor resin is desirable. [a metal alkoxide,]

[0034] As a metal alkoxide in this invention, the silicon alkoxide shown in a general formula 1 and/or its condensate are used. Although metal alkoxides, such as Ti, aluminum, and Zr, are also possible, when it uses the alkoxides of Si, or Si as a principal component and also the mixture of metal alkoxides is used as other metal alkoxides, the reaction rate of hydrolysis and a polycondensation is loose, and it is desirable especially when controlling a concentration inclination.

[0035] The highest part of the content (it may only be hereafter called metallic-oxide content) in the inside of the complex of a metallic-oxide component (A) is 5 - 100 % of the weight, and, as for the component inclination complex of the organic macromolecule and metallic oxide in this invention, what is 0 - 50 % of the weight in the lowest part is desirable.

[0036] It becomes, and limit that that it is easy to produce generating of a crack etc. the thickness of the whole complex must be very thin etc. becomes [**** / that complex becomes weak] large, and that to which the metallic-oxide content in the lowest part exceeds [the metallic-oxide content in the highest part] 50 % of the weight insufficiently [less than 5 % of the weight / the effectiveness of compound-izing] is not desirable.

[0037] Moreover, the ratio of the highest place of metallic-oxide content and a low place needs to be two or more preferably 1.5 or more. As for the effectiveness as component inclination complex, less than 1.5 are [the ratio concerned] insufficient. Moreover, when the thickness (d1) from which metallic-oxide concentration is changing in the depth direction in inclination is larger than the thickness (d2) of the field which shows the highest metallic-oxide content, the effectiveness as inclination composite is more clear.

[0038] As magnitude of the metallic oxide in this invention, it is 0.01 micrometers - 5 micrometers in diameter. When the organic macromolecule which especially the magnitude of a metallic oxide uses by 0.01 micrometers - 0.5 micrometers is transparent, the complex of this invention has the appearance of transparence - translucence. Moreover, when the magnitude of a metallic oxide is 0.5 micrometers - 5 micrometers, it has the appearance of translucent - opacity.

[0039] Anyway, compared with carrying out mixed distribution of the metallic-oxide particle manufactured beforehand and the organic macromolecule in the component inclination complex which consists of a metallic oxide which is made to carry out the polycondensation of a metal alkoxide or its condensate under organic macromolecule existence, and is obtained, and an organic macromolecule, particle-size control of a metallic-oxide particle is easy to the diameter of a microscopic granule.

[0040] the possibility of the homogeneity distribution of even a thing with a diameter of about 1-2 micrometers as particles for reinforcement addition, such as the conventional silica, — moreover, it sees in cost and has become the limitation. When using a still smaller particle, homogeneous distribution or its control is difficult by condensation of a consistency difference with an organic macromolecule, or a particle in many cases.

[0041] In this invention, the mean particle diameter of a metallic oxide is contained in homogeneity to the thing of NANOME-TA-size, and the component inclination complex by which decentralized-structure control was carried out can be obtained. In measurement by a **** type electron microscope etc., since it is difficult for the magnitude of the metallic oxide in this invention to catch the particle size of 0.01 micrometers or less, it attaches the numeric value of 0.01 micrometers, but even if it is smaller than 0.01 micrometers, it does not interfere at all. However, component inclination complex with mean particle diameter homogeneous in 5 micrometers or more becomes is hard to be obtained.

[0042] While the component inclination complex finally obtained maintains distribution homogeneous in micro as an approach of obtaining the component inclination complex of the organic macromolecule of this invention, and a metallic oxide, it is not limited in the depth direction of complex especially by the manufacture approach that what is necessary is just what has the field where metallic-oxide concentration changes continuously.

[0043] However, if an example of the concrete manufacture approach is given, in case hydrolysis and the polycondensation of a metal alkoxide, the hardening reaction of resin, and/or the solvent cast are made to perform using an organic macromolecule component and a metal alkoxide or its condensate, water, a catalyst, and/or an organic solvent as a raw material, actuation which produces hydrolysis and the polycondensation of uneven metal alkoxides in the depth direction of the complex finally obtained will be performed, for example.

[0044] Furthermore, it is possible by giving concentration distribution of a specific raw material component (for example, a metal alkoxide, a basic catalyst, and water) in the depth direction among the above-mentioned raw materials, or specifically performing the external stimulus (for example, heating) from an one direction to make inclination metallic-oxide concentration distribution discover.

[0045] For example, after holding what applied the homogeneity solution which consists of an organic macromolecule, a metal alkoxide or its condensate, those common solvents, and/or a polymerization catalyst of a metal alkoxide on the base material under the ambient atmosphere which makes it come in air to contain the polymerization catalyst and/or organic solvent of water and/or a metal alkoxide, the inclination of the metallic-oxide concentration in the inside of a paint film can be made to discover by performing desiccation and heat treatment.

[0046] In this invention, although the acid or alkali the same as a polymerization catalyst of a metal alkoxide or of a different kind contained in an ambient atmosphere or a homogeneity solution is used, it is desirable in the atomization and component inclination control of a metallic oxide in inclination complex especially to use an alkali like various amine compounds or ammonia.

[0047] Moreover, what mixes with homogeneity with the solution which consists of an organic macromolecule etc.

as an organic solvent contained in an ambient atmosphere in this invention is desirable, and, as for the organic solvent already contained in the solution, it is desirable that it is especially the thing of a different class.
[0048] The component inclination complex of the organic macromolecule of this invention and a metallic oxide can be used for various Plastic solids and shaping raw materials, such as a paint film, yarn, a film, and a particle. Moreover, it is also possible to prepare by the system containing organic fiber, such as an inorganic fiber and/or celluloses, such as other metals and glass, and aramid, and/or those powder.
[0049] What has 5 - 100 % of the weight and high metallic-oxide concentration in at least one surface section, for example although the average concentration of the metallic oxide of the whole complex is very low, and has the structure of the distributed condition which the concentration is dwindling in inclination, applying to the interior from the surface section in the component inclination complex of the organic macromolecule of this invention and a metallic oxide is possible.
[0050] Therefore, although it has the property by only the surface section having more high metallic-oxide concentration in this case, for example, a high degree of hardness and the outstanding solvent resistance, and thermal resistance Since it is limited to fixed thickness from a front face (for example, since it is in component inclination, the degradation factor by a crack etc. not being seen and applying [the] it to the interior), it can discover the composite property stabilized as exfoliation of only a surface side arose neither by heating nor aging. On the contrary, what has internal metallic-oxide concentration higher than the surface section, and the thing which shows multilayer concentration distribution more intricately are also possible.
[0051]
[Example] Subsequently, an example explains this invention further. In addition, % in an example is weight criteria as long as there is no notice especially.
[0052] (Example 1) 30g (Dainippon Ink & Chemicals [, Inc.] make: AKURIDIKKU A-405) (57% of pitches; a xylene, butanol solution) of acrylic resin, 6.5g (Dainippon Ink & Chemicals [, Inc.] make: super BEKKAMIN G-821) (60% of pitches; isobutyl solution) of melamine resin, 2.5g (Dainippon Ink & Chemicals [, Inc.] make: Epiclon 1050) of epoxy resins, a tetramethoxy silane (hereafter referred to as TMOS.) : The Tokyo Chemicals industrial company make They are 10g of reagent chemicals, and the homogeneity solution which consists of dehydration tetrahydrofuran (THF; reagent chemicals by Kanto chemistry incorporated company) 20g [0053] After being dropped on the base material (Nylon 66 plate) and leaving it for about 5 hours under the saturated steam ambient atmosphere of 0.09 mols [/l.] ammonia concentration, it was further left for about one day to 28 degrees C and 50%. The paint film (about 40-micron thickness) which performs at 80 degrees C for 2 hours, performs heat treatment at 150 more degrees C for 1 hour, and consists of acrylic resin / a silica system was obtained.
[0054] The result of having scanned distribution of Si of the cross section of a paint film from the front face is shown in drawing 1 using an electron probe microanalyzer (EPMA). It is admitted that distribution of Si strong against a front-face side is seen, and it crosses in the depth direction which is about 40 microns, and Si concentration is changing continuously from the result of drawing 1 .
[0055] Moreover, in the depth direction and the direction of a right angle, the fact that the same distribution was shown even if it measures Si concentration distribution of this depth direction in the location of several places where the same paint films differ showed holding homogeneous Si concentration. From the above result, the obtained paint film had the silica content layer of high concentration in the surface section from the average metallic-oxide concentration of the whole paint film, and it was homogeneously checked in the depth direction in the depth direction and the direction of a right angle that it is the complex (paint film) which has a continuous concentration change. It is here and is [0056]. Thickness of a concentration inclination field = it was about 23 micrometers, and the concentration inclination field thickness / [whole] thickness =0.54 concentration inclination field thickness / maximum concentration field thickness = abbreviation 9 maximum metallic-oxide concentration / minimum metallic-oxide concentration =28 % of the weight / 3.5 % of the weight =7.3.
[0057] This component inclination complex was presenting thin nebula, and when the paint film cross section was observed using the scanning electron microscope (SEM), the silica particle of magnitude with a diameter of 0.2-0.4 micrometers was observed. Although the condition of distribution of a silica particle was homogeneous, it was highly distributed near the paint film front face, and it was falling as it went to the interior of a paint film.
[0058] In addition, EPMA performed output [of 15kV]-50nA, resolution of 1-1.5 microns, 10-micron scan speed for /, and detection by K alpha rays (7.126A) of Si using EPM-810 mold by Shimadzu Corp. Moreover, SEM observed by the sample which carried out sputtering of about 3nm platinum using ohm SUTORONGU SEM of S-800 mold by Hitachi, Ltd.
[0059] (Example 2) In the manufacture conditions of an example 1, the case where it carried out under 25 degrees C and 50% of ambient atmosphere was examined instead of using methanol 20g instead of THF20g, and performing the cast of a homogeneity solution in the saturated steam of aqueous ammonia further. The paint film excellent in transparency was obtained. The result of EPMA measurement is shown in drawing 2 . It turns out that the base side serves as component inclination complex which has high metallic-oxide concentration.
[0060] Thickness =40micrometer, the concentration inclination field thickness / [whole] thickness =0.7 concentration inclination field thickness / maximum concentration field thickness =10 maximum metallic-oxide concentration / minimum metallic-oxide concentration =11.5 % of the weight / 4.5% of the weight of a concentration inclination field = it was 2.5.
[0061] Component inclination complex was transparent and it was observed in SEM observation that the particle with a diameter of about 0.04-0.1 micrometers is distributing to homogeneity in the micro range.
[0062] (Example 1 of a comparison) The same technique as an example 1 examined by creating a sample using the

homogeneity solution which adds 5g distilled water in the homogeneity solution of an example 1, and is obtained. The result of EPMA measurement is shown in drawing 3 . An inclination is not looked at by silica concentration and it turns out that it is distributed over homogeneity.
[0063] Thickness of a concentration inclination field = 0 micrometer, and the maximum metallic-oxide concentration / minimum metallic-oxide concentration =12 % of the weight / 11 % of the weight =1.1 complex were transparent, and it was checked in SEM observation that the particle with a diameter of 0.06-0.15 micrometers is distributing to homogeneity.
[0064] (Example 2 of a comparison) The case where ammonia concentration of the aqueous ammonia in an example 1 was carried out in 0.5 mols/l. was examined by preparing a sample by the same approach as an example 1. The result of EPMA measurement is shown in drawing 4 . An inclination is not looked at by silica concentration and it turns out that it is distributed over homogeneity.
[0065] Thickness =0micrometer, the maximum metallic-oxide concentration / minimum metallic-oxide concentration =13.5 % of the weight / 12.5% of the weight of a concentration inclination field = complex was the transparent body in 1.1.
[0066] (Example 3) After dropping the same homogeneity solution as an example 1 on the Nylon 66 plate and leaving it at 22 degrees C for about 10 hours under the saturated steam ambient atmosphere of 10:3 (weight ratio) mixed solution of 0.06 mols [/l.] aqueous ammonia and a methanol, the paint film (about 75-micron thickness) which performs the same processing as an example 1, and consists of acrylic resin / a silica system was obtained. The result of EPMA measurement is shown in drawing 5 . It turns out that the inclination complex which has very high silica concentration in a paint film front-face side is obtained.
[0067] Concentration inclination field thickness = 40 micrometers, and the concentration inclination field thickness / [whole] thickness =0.53 concentration inclination field thickness / maximum concentration field thickness =13.3 maximum metallic-oxide concentration / minimum metallic-oxide concentration =30 % of the weight / 3 % of the weight =10 inclination complex are presenting nebula, and it was observed in SEM observation that the particle with a diameter of about 0.3-2 micrometers is distributing to homogeneity in the micro range.
[0068] (Example 4) The paint film (about 120-micron thickness) which heat-treats with the solvent cast on the same conditions as an example 3, and consists of acrylic resin / a silica system was obtained using the homogeneity solution which adds 0.06 moreg triethylamine (Tokyo formation industrial incorporated company make, reagent chemicals), and is obtained by the same homogeneity solution as an example 1. The result of EPMA measurement is shown in drawing 6 . It turns out that the paint film front-face side serves as inclination complex which has high silica concentration.
[0069] Concentration inclination field thickness =70micrometer, the concentration inclination field thickness / [whole] thickness =0.58 concentration inclination field thickness / maximum concentration field thickness =17.5 maximum metallic-oxide concentration / minimum metallic-oxide concentration =40 % of the weight / 7.5 % of the weight = 5.3 [0070] Compared with the complex of an example 3, the concentration inclination of a metallic oxide is gently-sloping. Inclination complex is presenting thin nebula and it was observed in SEM observation that the particle with a diameter of about 60-200nm is distributing to homogeneity in the micro range. Compared with the complex of an example 3, the particulate material with a small particle size was obtained.
[0071] (Example 5) After carrying out mixed stirring of 10g (Dainippon Ink & Chemicals [, Inc.] make: Epiclon 850) of bisphenol mold epoxy resins, 2g (Dainippon Ink & Chemicals [, Inc.] make: Epiclon B-053) of aliphatic series polyamine system epoxy curing agents, and the mixed solution of THF 5g at a room temperature for 26 hours, 5g TMOS was mixed to homogeneity. The obtained homogeneity sol solution was applied to the substrate, the solvent cast was carried out at the room temperature (18 degrees C, 40%), it performed at 80 degrees C for 5 hours, heat treatment was performed at 150 degrees C for 3 hours, and the complex of an epoxy resin and a silica was obtained. The result of EPMA measurement is shown in drawing 7 . It turns out that the interior of about 50 micrometers on the front face of a paint film serves as inclination complex of a gestalt with which silica concentration serves as max.
[0072] Concentration inclination field thickness =170micrometer, concentration inclination field thickness / [whole] thickness =0.7, concentration inclination field thickness / maximum concentration field thickness =8.5, the maximum metallic-oxide concentration / minimum metallic-oxide concentration =26.5 % of the weight / 10.0 % of the weight = it was 2.65. Inclination complex is homogeneity transparence and it was observed in SEM observation that the particle with a diameter of about 30-200nm is distributing to homogeneity in the micro range.
[0073] (Example 6) 15g (Dainippon Ink & Chemicals [, Inc.] make: BEKKOZORU 1343) of alkyd resin, 5g (Dainippon Ink & Chemicals [, Inc.] make: super BEKKAMIN G-821-60) of butylated melamine resin, ethanol The mixed solution of 10g and TMOS 5g was stirred, and the homogeneity sol solution was obtained. After applying the obtained homogeneity sol solution to the substrate and carrying out the solvent cast under the ambient atmosphere of 0.4 mols [/l.] aqueous ammonia (30 degrees C), it performed at 80 degrees C for 5 hours, heat treatment was performed at 150 degrees C for 1 hour, and the complex of alkyd resin and a silica was obtained. The result of EPMA measurement is shown in drawing 8 . It turns out that the paint film surface section serves as inclination complex of a gestalt with which silica concentration serves as max. The inclination is formed over the whole thickness (about 120 micrometers), and was formed into milk nebula.
[0074] Concentration inclination field thickness =120micrometer, concentration inclination field thickness / [whole] thickness =1, more than [more than concentration inclination field thickness / maximum concentration field thickness =120], the maximum metallic-oxide concentration / minimum metallic-oxide concentration =62 % of the weight / 14 % of the weight = it was 4.4.

[0075]
[Effect of the Invention] The component inclination complex of the organic macromolecule and metallic oxide which are obtained by this invention Since it distributes so that homogeneity may be made to distribute the metallic oxide of various magnitude extremely in an organic macromolecule (from micrometer order to about 10nm) and the content concentration of a metallic oxide may have distribution in the thickness direction of the complex concerned, For example, manufacture of the complex which has the part which has metallic-oxide concentration higher (low) than the average concentration of the metallic oxide in the whole complex in the surface section or the interior is possible. When it has the physical properties containing quantity (or low) metallic-oxide concentration peculiar to organic macromolecule complex and metallic-oxide concentration is changing in inclination, stable composite which exfoliation of a surface side and the interior produces neither by heating nor aging like a general paint film can be offered.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the component inclination complex and its manufacturing method of the organic macromolecule and metallic oxide which are characterized by having the field where the content of a metallic oxide differs in inclination in the thickness direction of complex in the complex of the metallic oxide and the organic macromolecule which are obtained by hydrolysis and the polycondensation reaction of a metal alkoxide.

[Translation done.]

PRIOR ART

[Description of the Prior Art] In order to reform the engine performance of an organic macromolecule, the resin which the approach of former versatility is examined, blends two or more organic macromolecules, and has a new property is prepared, or preparing the Plastic solid which compound-izes with reinforcing materials of a different kind, and has the target property etc. is performed widely.
[0003] For example, by blend compound-ization of organic giant molecules, it considers as homogeneous complex by approaches, such as melting mixing, and reforming of the organic giant molecule according to the purpose of use has been made by devising and blending mixed conditions etc. so that it may have the specific decentralized structure which looks for the organic giant molecule in which compatibility is shown, and includes microfacies isolation construction for the organic giant molecule which is immiscible nature.
[0004] On the other hand, physical-properties reforming by making an organic macromolecule mix and distribute reinforcement is also examined broadly. Specifically mixing powdered inorganic materials, such as a fibrous material organic [, such as an aramid fiber, pulp, a glass fiber, and a carbon fiber,] or inorganic, a calcium carbonate, a silica, and an alumina, etc. with an organic macromolecule is performed widely.
[0005] Compound-ization especially by mixing with an inorganic material has been widely considered as an easy high performance reforming means from the ability of the thermal resistance which was excellent in the inorganic material, or a mechanical property to be employed efficiently. However, in the case of an inorganic material, it is common to be compound-ized for the purpose of it not being easy to control a distributed condition micro, and obtaining the most homogeneous chiefly possible bulk composite material from the difference in an essential property with the organic polymeric materials in points, such as the thermal infusibility, chemical insolubility, high specific gravity, and a surface characteristic.
[0006] That is, in order to raise the reforming effectiveness, it has a smaller configuration, and a wettability good thing with a matrix macromolecule is chosen as an inorganic material for reinforcement, and it has become an important factor in compound-izing that only the specified quantity distributes them to homogeneity as much as possible. However, even in this case, an inorganic material has the problem which homogeneity distribution becomes difficult and becomes energy and what is high also in cost, so that it becomes particle-like.
[0007] Therefore, in order to obtain the composite of the organic material of the high performance which consists of an organic material and a particle-like inorganic material and by which it was homogeneous in micro and the decentralized structure was controlled, and an inorganic material, it is completely difficult and a new technique needs to be developed of the above approaches of only mixing a particle-like inorganic material with an organic macromolecule.
[0008] this invention persons have performed development research of the composite of effective new organic material and non-equipments to such a purpose. As the example, there are micro hybrid composites of the metallic oxide and the organic giant molecule which are obtained for example, from a metal alkoxide.
[0009] It is the composite material of the organic material which the wettability of the metallic-oxide particle of MIKURONO-DA [from NANOO-DA -] - is good in an organic macromolecule by performing hydrolysis and the polycondensation of a metal alkoxide by in-situ in an organic macromolecule matrix, and this complex is compound [distribution and]-ized by homogeneity, and has the properties which were very excellent including a mechanical property, and non-equipments.
[0010] However, if the metallic-oxide component rate in this complex is enlarged too much, good composite will no longer be obtained according to the difference of the essential property of the organic macromolecule and metallic oxide which are compound-ized. That is, in what has high metallic-oxide content, that it is easy to produce a crack, become, become weak, a moldability worsens, and deformation of curvature, distortion, etc. is produced. On the other hand, by the thing of a minute amount, desired composite nature is no longer obtained for metallic-oxide content.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] The component inclination complex of the organic macromolecule and metallic oxide which are obtained by this invention Since it distributes so that homogeneity may be made to distribute the metallic oxide of various magnitude extremely in an organic macromolecule (from micrometer order to about 10nm) and the content concentration of a metallic oxide may have distribution in the thickness direction of the complex concerned, For example, manufacture of the complex which has the part which has metallic-oxide concentration higher (low) than the average concentration of the metallic oxide in the whole complex in the surface section or the interior is possible. When it has the physical properties containing quantity (or low) metallic-oxide concentration peculiar to organic macromolecule complex and metallic-oxide concentration is changing in inclination, stable composite which exfoliation of a surface side and the interior produces neither by heating nor aging like a general paint film can be offered.

[Translation done.]

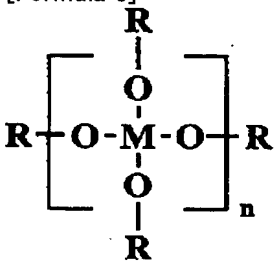
TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The technical problem which this invention tends to solve is obtaining the good complex which may discover effectively the property to the high content field of a metallic oxide, and is to offer the component inclination complex and its manufacturing method of the organic macromolecule and metallic oxide which have a good moldability which a crack cannot more specifically produce easily and exfoliation of only a surface side produces neither by heating nor aging.

[Translation done.]

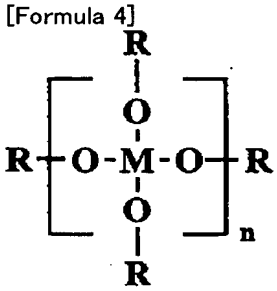
MEANS

[Means for Solving the Problem] In the complex which consists of an organic macromolecule and a metallic oxide, this invention person etc. tackles research wholeheartedly so that he may get the complex which has the property which was excellent in the wide range presentation field, and he comes to complete this research.
[0013] Namely, this invention is the complex of the organic macromolecule and metallic oxide containing an organic macromolecule component and at least two sorts of components of a metallic-oxide component (A). The content in the inside of the complex of a metallic-oxide component (A) changes in the depth direction from the front face of complex continuously. It has component inclination structure and is the component inclination complex of the organic macromolecule and metallic oxide which are 0 - 50 % of the weight, and are characterized by the ratio of the content of a high place and a low place being 1.5 or more in 5 - 100 % of the weight, and the lowest location in the location where the content concerned is the highest.
[0014] The component inclination complex of the organic macromolecule of this invention and a metallic oxide is component inclination complex of the organic macromolecule and metallic oxide with which the metallic-oxide component (A) is characterized by being obtained under existence of an organic macromolecule component according to a metal alkoxide, or its hydrolysis and polycondensation of a low condensate in detail.
[0015] Moreover, the component inclination complex of the organic macromolecule of this invention and a metallic oxide is detailed, and it is characterized by the metallic-oxide component (A) existing in at least one front face of complex exceeding the average content in the whole complex.
[0016] Furthermore, the component inclination complex of the organic macromolecule of this invention and a metallic oxide is component inclination complex of the organic macromolecule and metallic oxide with which a metallic-oxide component (A) is characterized by existing by the ratio below the average content in the whole complex in at least one front face of complex.
[0017] Moreover, the component inclination complex of the organic macromolecule of this invention and a metallic oxide is component inclination complex of the organic macromolecule and metallic oxide which are characterized by the thickness (d1) from which the content of a metallic-oxide component (A) is changing continuously being larger than the thickness (d2) which shows the highest content of a metallic-oxide component (A) in the depth direction of complex.
[0018] Furthermore, the component inclination complex of the organic macromolecule of this invention and a metallic oxide contains the component inclination complex of the component inclination complex of the organic macromolecule and metallic oxide with which magnitude of the metallic oxide in complex is characterized by being the pitch diameter of 0.01-5 micrometers, and the organic macromolecule and metallic oxide with which magnitude of the metallic oxide in complex is characterized by being the pitch diameter of 0.01-0.5 micrometers.
[0019] Moreover, the component inclination complex of the organic macromolecule of this invention and a metallic oxide is component inclination complex of the organic macromolecule and metallic oxide which are characterized by being what the metallic-oxide component is obtained under existence of an organic macromolecule component according to a metal alkoxide, or its hydrolysis and polycondensation of a low condensate, and the metal alkoxide or its condensate is especially expressed with a general formula 1 to.
[0020] (General formula 1)
[Formula 3]



(Among a formula, in M, CmH2m+1 and m express the integer of 1-4, and, as for n, a silicon atom and R express the integer of 1-10.)
[0021] Moreover, the component inclination complex of the organic macromolecule of this invention and a metallic oxide is component inclination complex of the organic macromolecule and metallic oxide which are characterized by an organic macromolecule component being thermosetting resin.

[0022] Moreover, the component inclination complex of the organic macromolecule of this invention and a metallic oxide is component inclination complex of the organic macromolecule and metallic oxide which are characterized by an organic macromolecule component being thermoplastics.
[0023] This invention includes the manufacture approach of the component inclination complex of the organic macromolecule and the metallic oxide which are characterized by performing desiccation and heat treatment, after holding what applied the homogeneity solution which consists of an organic macromolecule, metal alkoxides, those common solvents, and/or a polymerization catalyst of a metal alkoxide on the organic macromolecule or the inorganic base material under the ambient atmosphere which included the polymerization catalyst and/or organic solvent of water and/or a metal alkoxide in air.
[0024] The manufacture approach of the component inclination complex of the organic macromolecule of this invention and a metallic oxide is a manufacturing method of the component component inclination complex of the organic macromolecule and the metallic oxide which are characterized by being the silicon alkoxide with which the metallic-oxide component distributes to homogeneity, and is obtained in an organic macromolecule component under existence of an organic macromolecule component according to a metal alkoxide, or its hydrolysis and polycondensation of a low condensate, and especially a metal alkoxide is indicated to be by the general formula 1, or its low condensate.
[0025] (General formula 1)
[Formula 4]



(Among a formula, in M, CmH2m+1 and m express the integer of 1-4, and, as for n, a silicon atom and R express the integer of 1-10.)
[0026] Moreover, especially the manufacture approach of the component inclination complex of the organic macromolecule of this invention and a metallic oxide includes the manufacture approach of the component inclination complex of the organic macromolecule and metallic oxide which are characterized by using congener or an alkali of a different kind as a polymerization catalyst of the metal alkoxide contained in an ambient atmosphere and/or a homogeneity solution.
[0027] That is, this invention is forming the component inclination structure where exist by the concentration from which the metallic-oxide component to contain differs in the interior of complex in the complex of the organic macromolecule per sort [at least], the organic macromolecule containing a metallic oxide, and a metallic oxide, and metallic-oxide constituent concentration changes in the depth direction from the front face of complex continuously, and [0028]. And the metallic-oxide constituent concentration in complex is 0 - 50 % of the weight in 5 - 100 % of the weight, and the lowest place in the highest place, And it is a thing about the component inclination complex of the organic macromolecule and metallic oxide which are characterized by the ratio of the content of a high place and a low place being 1.5 or more. It centers on the component inclination complex of the organic macromolecule and metallic oxide which consist of a metallic oxide especially obtained under organic macromolecule existence by carrying out the polycondensation of a metal alkoxide or its low condensate, and an organic macromolecule.
[0029] In the component inclination complex of the organic macromolecule and a metallic oxide concerned, that whose metallic-oxide component is below the average metallic-oxide concentration of complex is included in at least one front face of complex in the thing in which the metallic-oxide component exists exceeding the average metallic-oxide concentration of complex, or at least one front face. Moreover, the component inclination complex of the organic macromolecule and a metallic oxide concerned contains what has the larger thickness which has a metallic-oxide concentration inclination than the thickness which has the highest content of a metallic oxide in the depth direction.
[0030] Moreover, the component inclination complex of the organic macromolecule and a metallic oxide concerned contains that whose magnitude of the metallic oxide contained in complex is the pitch diameter of 0.01 micrometers - 5 micrometers. Moreover, the gestalt is a paint film, yarn, a film, and a spherical thing, and also the component inclination complex of the organic macromolecule and a metallic oxide concerned contains what is the Plastic solid of various configurations, such as a block.
[0031] In this invention, while a metallic oxide maintains homogeneity into an organic macromolecule except the depth direction, it is based on having the field which is changing in the depth direction continuously. Therefore, it differs in what has the field where metallic-oxide concentration differs nonsequetially by only irregular condensation and phase separation, the thing which has the homogeneity paint film which has the fixed metallic-oxide content formed of paint on the front face of a base material.
[0032] As an organic macromolecule which can be used for this invention, according to the polycondensation of the metal alkoxide under organic macromolecule existence Although not limited especially, just possible [building the

complex of a homogeneous organic macromolecule and a homogeneous metallic oxide] specifically For example, phenol resin, an epoxy resin, acrylic resin, alkyd resin, Thermosetting resin, such as melamine resin and a urea-resin, nylon, polyester, It is possible to use thermoplastics, such as acrylic resin, polybutadiene, rubber system resin like SBS, etc., and an epoxy resin, acrylic resin, alkyd resin, and melamine resin are especially desirable also in thermosetting resin.

[0033] What is the organic macromolecule which dissolves in the homogeneity solution which consists of its condensate, them, a solvent, etc. in the viewpoint from the ease on manufacture, or is swollen, or its precursor resin is desirable. [a metal alkoxide,]

[0034] As a metal alkoxide in this invention, the silicon alkoxide shown in a general formula 1 and/or its condensate are used. Although metal alkoxides, such as Ti, aluminum, and Zr, are also possible, when it uses the alkoxides of Si, or Si as a principal component and also the mixture of metal alkoxides is used as other metal alkoxides, the reaction rate of hydrolysis and a polycondensation is loose, and it is desirable especially when controlling a concentration inclination.

[0035] The highest part of the content (it may only be hereafter called metallic-oxide content) in the inside of the complex of a metallic-oxide component (A) is 5 - 100 % of the weight, and, as for the component inclination complex of the organic macromolecule and metallic oxide in this invention, what is 0 - 50 % of the weight in the lowest part is desirable.

[0036] It becomes, and limit that that it is easy to produce generating of a crack etc. the thickness of the whole complex must be very thin etc. becomes [**** / that complex becomes weak] large, and that to which the metallic-oxide content in the lowest part exceeds [the metallic-oxide content in the highest part] 50 % of the weight insufficiently [less than 5 % of the weight / the effectiveness of compound-izing] is not desirable.

[0037] Moreover, the ratio of the highest place of metallic-oxide content and a low place needs to be two or more preferably 1.5 or more. As for the effectiveness as component inclination complex, less than 1.5 are [the ratio concerned] insufficient. Moreover, when the thickness (d1) from which metallic-oxide concentration is changing in the depth direction in inclination is larger than the thickness (d2) of the field which shows the highest metallic-oxide content, the effectiveness as inclination composite is more clear.

[0038] As magnitude of the metallic oxide in this invention, it is 0.01 micrometers - 5 micrometers in diameter. When the organic macromolecule which especially the magnitude of a metallic oxide uses by 0.01 micrometers - 0.5 micrometers is transparent, the complex of this invention has the appearance of transparence - translucence. Moreover, when the magnitude of a metallic oxide is 0.5 micrometers - 5 micrometers, it has the appearance of translucent - opacity.

[0039] Anyway, compared with carrying out mixed distribution of the metallic-oxide particle manufactured beforehand and the organic macromolecule in the component inclination complex which consists of a metallic oxide which is made to carry out the polycondensation of a metal alkoxide or its condensate under organic macromolecule existence, and is obtained, and an organic macromolecule, particle-size control of a metallic-oxide particle is easy to the diameter of a microscopic granule.

[0040] the possibility of the homogeneity distribution of even a thing with a diameter of about 1-2 micrometers as particles for reinforcement addition, such as the conventional silica, — moreover, it sees in cost and has become the limitation. When using a still smaller particle, homogeneous distribution or its control is difficult by condensation of a consistency difference with an organic macromolecule, or a particle in many cases.

[0041] In this invention, the mean particle diameter of a metallic oxide is contained in homogeneity to the thing of NANOME-TA-size, and the component inclination complex by which decentralized-structure control was carried out can be obtained. In measurement by a **** type electron microscope etc., since it is difficult for the magnitude of the metallic oxide in this invention to catch the particle size of 0.01 micrometers or less, it attaches the numeric value of 0.01 micrometers, but even if it is smaller than 0.01 micrometers, it does not interfere at all. However, component inclination complex with mean particle diameter homogeneous in 5 micrometers or more becomes is hard to be obtained.

[0042] While the component inclination complex finally obtained maintains distribution homogeneous in micro as an approach of obtaining the component inclination complex of the organic macromolecule of this invention, and a metallic oxide, it is not limited in the depth direction of complex especially by the manufacture approach that what is necessary is just what has the field where metallic-oxide concentration changes continuously.

[0043] However, if an example of the concrete manufacture approach is given, in case hydrolysis and the polycondensation of a metal alkoxide, the hardening reaction of resin, and/or the solvent cast are made to perform using an organic macromolecule component and a metal alkoxide or its condensate, water, a catalyst, and/or an organic solvent as a raw material, actuation which produces hydrolysis and the polycondensation of uneven metal alkoxides in the depth direction of the complex finally obtained will be performed, for example.

[0044] Furthermore, it is possible by giving concentration distribution of a specific raw material component (for example, a metal alkoxide, a basic catalyst, and water) in the depth direction among the above-mentioned raw materials, or specifically performing the external stimulus (for example, heating) from an one direction to make inclination metallic-oxide concentration distribution discover.

[0045] For example, after holding what applied the homogeneity solution which consists of an organic macromolecule, a metal alkoxide or its condensate, those common solvents, and/or a polymerization catalyst of a metal alkoxide on the base material under the ambient atmosphere which makes it come in air to contain the polymerization catalyst and/or organic solvent of water and/or a metal alkoxide, the inclination of the metallic-oxide concentration in the inside of a paint film can be made to discover by performing desiccation and heat

treatment.
[0046] In this invention, although the acid or alkali the same as a polymerization catalyst of a metal alkoxide or of a different kind contained in an ambient atmosphere or a homogeneity solution is used, it is desirable in the atomization and component inclination control of a metallic oxide in inclination complex especially to use an alkali like various amine compounds or ammonia.
[0047] Moreover, what mixes with homogeneity with the solution which consists of an organic macromolecule etc. as an organic solvent contained in an ambient atmosphere in this invention is desirable, and, as for the organic solvent already contained in the solution, it is desirable that it is especially the thing of a different class.
[0048] The component inclination complex of the organic macromolecule of this invention and a metallic oxide can be used for various Plastic solids and shaping raw materials, such as a paint film, yarn, a film, and a particle. Moreover, it is also possible to prepare by the system containing organic fiber, such as an inorganic fiber and/or celluloses, such as other metals and glass, and aramid, and/or those powder.
[0049] What has 5 - 100 % of the weight and high metallic-oxide concentration in at least one surface section, for example although the average concentration of the metallic oxide of the whole complex is very low, and has the structure of the distributed condition which the concentration is dwindling in inclination, applying to the interior from the surface section in the component inclination complex of the organic macromolecule of this invention and a metallic oxide is possible.
[0050] Therefore, although it has the property by only the surface section having more high metallic-oxide concentration in this case, for example, a high degree of hardness and the outstanding solvent resistance, and thermal resistance Since it is limited to fixed thickness from a front face (for example, since it is in component inclination, the degradation factor by a crack etc. not being seen and applying [the] it to the interior), it can discover the composite property stabilized as exfoliation of only a surface side arose neither by heating nor aging. On the contrary, what has internal metallic-oxide concentration higher than the surface section, and the thing which shows multilayer concentration distribution more intricately are also possible.

[Translation done.]

EXAMPLE

[Example] Subsequently, an example explains this invention further. In addition, % in an example is weight criteria as long as there is no notice especially.
[0052] (Example 1) 30g (Dainippon Ink & Chemicals [, Inc.] make: AKURIDIKKU A-405) (57% of pitches; a xylene, butanol solution) of acrylic resin, 6.5g (Dainippon Ink & Chemicals [, Inc.] make: super BEKKAMIN G-821) (60% of pitches; isobutyl solution) of melamine resin, 2.5g (Dainippon Ink & Chemicals [, Inc.] make: Epiclon 1050) of epoxy resins, a tetramethoxy silane (hereafter referred to as TMOS.) : The Tokyo Chemicals industrial company make They are 10g of reagent chemicals, and the homogeneity solution which consists of dehydration tetrahydrofuran (THF; reagent chemicals by Kanto chemistry incorporated company) 20g [0053] After being dropped on the base material (Nylon 66 plate) and leaving it for about 5 hours under the saturated steam ambient atmosphere of 0.09 mols [/l.] ammonia concentration, it was further left for about one day to 28 degrees C and 50%. The paint film (about 40-micron thickness) which performs at 80 degrees C for 2 hours, performs heat treatment at 150 more degrees C for 1 hour, and consists of acrylic resin / a silica system was obtained.
[0054] The result of having scanned distribution of Si of the cross section of a paint film from the front face is shown in drawing 1 using an electron probe microanalyzer (EPMA). It is admitted that distribution of Si strong against a front-face side is seen, and it crosses in the depth direction which is about 40 microns, and Si concentration is changing continuously from the result of drawing 1 .
[0055] Moreover, in the depth direction and the direction of a right angle, the fact that the same distribution was shown even if it measures Si concentration distribution of this depth direction in the location of several places where the same paint films differ showed holding homogeneous Si concentration. From the above result, the obtained paint film had the silica content layer of high concentration in the surface section from the average metallic-oxide concentration of the whole paint film, and it was homogeneously checked in the depth direction in the depth direction and the direction of a right angle that it is the complex (paint film) which has a continuous concentration change. It is here and is [0056]. Thickness of a concentration inclination field = it was about 23 micrometers, and the concentration inclination field thickness / [whole] thickness =0.54 concentration inclination field thickness / maximum concentration field thickness = abbreviation 9 maximum metallic-oxide concentration / minimum metallic-oxide concentration =28 % of the weight / 3.5 % of the weight =7.3.
[0057] This component inclination complex was presenting thin nebula, and when the paint film cross section was observed using the scanning electron microscope (SEM), the silica particle of magnitude with a diameter of 0.2-0.4 micrometers was observed. Although the condition of distribution of a silica particle was homogeneous, it was highly distributed near the paint film front face, and it was falling as it went to the interior of a paint film.
[0058] In addition, EPMA performed output [of 15kV]-50nA, resolution of 1-1.5 microns, 10-micron scan speed for /, and detection by K alpha rays (7.126A) of Si using EPM-810 mold by Shimadzu Corp. Moreover, SEM observed by the sample which carried out sputtering of about 3nm platinum using ohm SUTORONGU SEM of S-800 mold by Hitachi, Ltd.
[0059] (Example 2) In the manufacture conditions of an example 1, the case where it carried out under 25 degrees C and 50% of ambient atmosphere was examined instead of using methanol 20g instead of THF20g, and performing the cast of a homogeneity solution in the saturated steam of aqueous ammonia further. The paint film excellent in transparency was obtained. The result of EPMA measurement is shown in drawing 2 . It turns out that the base side serves as component inclination complex which has high metallic-oxide concentration.
[0060] Thickness =40micrometer, the concentration inclination field thickness / [whole] thickness =0.7 concentration inclination field thickness / maximum concentration field thickness =10 maximum metallic-oxide concentration / minimum metallic-oxide concentration =11.5 % of the weight / 4.5% of the weight of a concentration inclination field = it was 2.5.
[0061] Component inclination complex was transparent and it was observed in SEM observation that the particle with a diameter of about 0.04-0.1 micrometers is distributing to homogeneity in the micro range.
[0062] (Example 1 of a comparison) The same technique as an example 1 examined by creating a sample using the homogeneity solution which adds 5g distilled water in the homogeneity solution of an example 1, and is obtained. The result of EPMA measurement is shown in drawing 3 . An inclination is not looked at by silica concentration and it turns out that it is distributed over homogeneity.
[0063] Thickness of a concentration inclination field = 0 micrometer, and the maximum metallic-oxide concentration / minimum metallic-oxide concentration =12 % of the weight / 11 % of the weight =1.1 complex were transparent, and it was checked in SEM observation that the particle with a diameter of 0.06-0.15 micrometers is distributing to homogeneity.

[0064] (Example 2 of a comparison) The case where ammonia concentration of the aqueous ammonia in an example 1 was carried out in 0.5 mols/l. was examined by preparing a sample by the same approach as an example 1. The result of EPMA measurement is shown in drawing 4 . An inclination is not looked at by silica concentration and it turns out that it is distributed over homogeneity.
[0065] Thickness =0micrometer, the maximum metallic-oxide concentration / minimum metallic-oxide concentration =13.5 % of the weight / 12.5% of the weight of a concentration inclination field = complex was the transparent body in 1.1.
[0066] (Example 3) After dropping the same homogeneity solution as an example 1 on the Nylon 66 plate and leaving it at 22 degrees C for about 10 hours under the saturated steam ambient atmosphere of 10:3 (weight ratio) mixed solution of 0.06 mols [/l.] aqueous ammonia and a methanol, the paint film (about 75-micron thickness) which performs the same processing as an example 1, and consists of acrylic resin / a silica system was obtained. The result of EPMA measurement is shown in drawing 5 . It turns out that the inclination complex which has very high silica concentration in a paint film front-face side is obtained.
[0067] Concentration inclination field thickness = 40 micrometers, and the concentration inclination field thickness / [whole] thickness =0.53 concentration inclination field thickness / maximum concentration field thickness =13.3 maximum metallic-oxide concentration / minimum metallic-oxide concentration =30 % of the weight / 3 % of the weight =10 inclination complex are presenting nebula, and it was observed in SEM observation that the particle with a diameter of about 0.3-2 micrometers is distributing to homogeneity in the micro range.
[0068] (Example 4) The paint film (about 120-micron thickness) which heat-treats with the solvent cast on the same conditions as an example 3, and consists of acrylic resin / a silica system was obtained using the homogeneity solution which adds 0.06 moreg triethylamine (Tokyo formation industrial incorporated company make, reagent chemicals), and is obtained by the same homogeneity solution as an example 1. The result of EPMA measurement is shown in drawing 6 . It turns out that the paint film front-face side serves as inclination complex which has high silica concentration.
[0069] Concentration inclination field thickness =70micrometer, the concentration inclination field thickness / [whole] thickness =0.58 concentration inclination field thickness / maximum concentration field thickness =17.5 maximum metallic-oxide concentration / minimum metallic-oxide concentration =40 % of the weight / 7.5 % of the weight = 5.3 [0070] Compared with the complex of an example 3, the concentration inclination of a metallic oxide is gently-sloping. Inclination complex is presenting thin nebula and it was observed in SEM observation that the particle with a diameter of about 60-200nm is distributing to homogeneity in the micro range. Compared with the complex of an example 3, the particulate material with a small particle size was obtained.
[0071] (Example 5) After carrying out mixed stirring of 10g (Dainippon Ink & Chemicals [, Inc.] make: Epiclon 850) of bisphenol mold epoxy resins, 2g (Dainippon Ink & Chemicals [, Inc.] make: Epiclon B-053) of aliphatic series polyamine system epoxy curing agents, and the mixed solution of THF 5g at a room temperature for 26 hours, 5g TMOS was mixed to homogeneity. The obtained homogeneity sol solution was applied to the substrate, the solvent cast was carried out at the room temperature (18 degrees C, 40%), it performed at 80 degrees C for 5 hours, heat treatment was performed at 150 degrees C for 3 hours, and the complex of an epoxy resin and a silica was obtained. The result of EPMA measurement is shown in drawing 7 . It turns out that the interior of about 50 micrometers on the front face of a paint film serves as inclination complex of a gestalt with which silica concentration serves as max.
[0072] Concentration inclination field thickness =170micrometer, concentration inclination field thickness / [whole] thickness =0.7, concentration inclination field thickness / maximum concentration field thickness =8.5, the maximum metallic-oxide concentration / minimum metallic-oxide concentration =26.5 % of the weight / 10.0 % of the weight = it was 2.65. Inclination complex is homogeneity transparence and it was observed in SEM observation that the particle with a diameter of about 30-200nm is distributing to homogeneity in the micro range.
[0073] (Example 6) 15g (Dainippon Ink & Chemicals [, Inc.] make: BEKKOZORU 1343) of alkyd resin, 5g (Dainippon Ink & Chemicals [, Inc.] make: super BEKKAMIN G-821-60) of butylated melamine resin, ethanol The mixed solution of 10g and TMOS 5g was stirred, and the homogeneity sol solution was obtained. After applying the obtained homogeneity sol solution to the substrate and carrying out the solvent cast under the ambient atmosphere of 0.4 mols [/l.] aqueous ammonia (30 degrees C), it performed at 80 degrees C for 5 hours, heat treatment was performed at 150 degrees C for 1 hour, and the complex of alkyd resin and a silica was obtained. The result of EPMA measurement is shown in drawing 8 . It turns out that the paint film surface section serves as inclination complex of a gestalt with which silica concentration serves as max. The inclination is formed over the whole thickness (about 120 micrometers), and was formed into milk nebula.
[0074] Concentration inclination field thickness =120micrometer, concentration inclination field thickness / [whole] thickness =1, more than [more than concentration inclination field thickness / maximum concentration field thickness =120], the maximum metallic-oxide concentration / minimum metallic-oxide concentration =62 % of the weight / 14 % of the weight = it was 4.4.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing showing Si distribution measurement result by the electron probe microanalyzer (EPMA) of the thickness direction of the component inclination complex (paint film) of the organic macromolecule and metallic oxide which were obtained in the example 1.
[Drawing 2] It is drawing showing Si distribution measurement result by EPMA of the thickness direction of the component inclination complex (paint film) of the organic macromolecule and metallic oxide which were obtained in the example 2.
[Drawing 3] It is drawing showing Si distribution measurement result by EPMA of the thickness direction of the complex (paint film) of the organic macromolecule and metallic oxide which were obtained in the example 1 of a comparison.
[Drawing 4] It is drawing showing Si distribution measurement result by EPMA of the thickness direction of the complex (paint film) of the organic macromolecule and metallic oxide which were obtained in the example 2 of a comparison.
[Drawing 5] It is drawing showing Si distribution measurement result by EPMA of the thickness direction of the component inclination complex (paint film) of the organic macromolecule and metallic oxide which were obtained in the example 3.
[Drawing 6] It is drawing showing Si distribution measurement result by EPMA of the thickness direction of the component inclination complex (paint film) of the organic macromolecule and metallic oxide which were obtained in the example 4.
[Drawing 7] It is drawing showing Si distribution measurement result by EPMA of the thickness direction of the component inclination complex (paint film) of the organic macromolecule and metallic oxide which were obtained in the example 5.
[Drawing 8] It is drawing showing Si distribution measurement result by EPMA of the thickness direction of the component inclination complex (paint film) of the organic macromolecule and metallic oxide which were obtained in the example 6.

[Translation done.]

* NOTICES *

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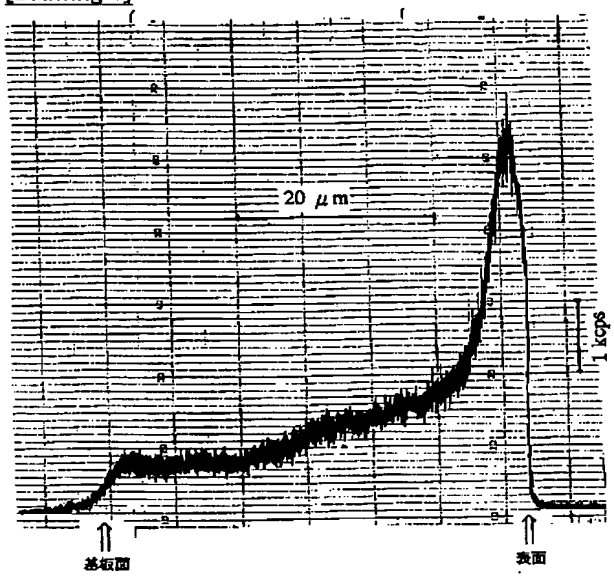
damages caused by the use of this translation.

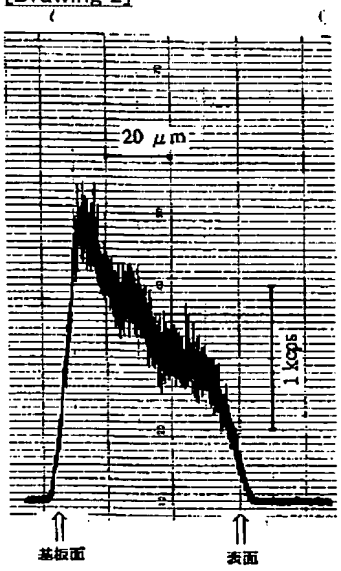
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

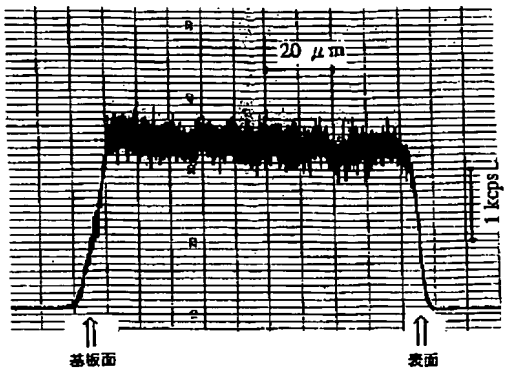
[Drawing 1]



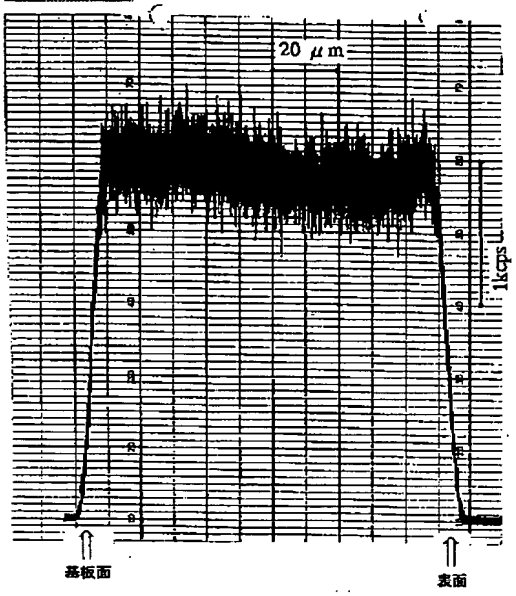
[Drawing 2]



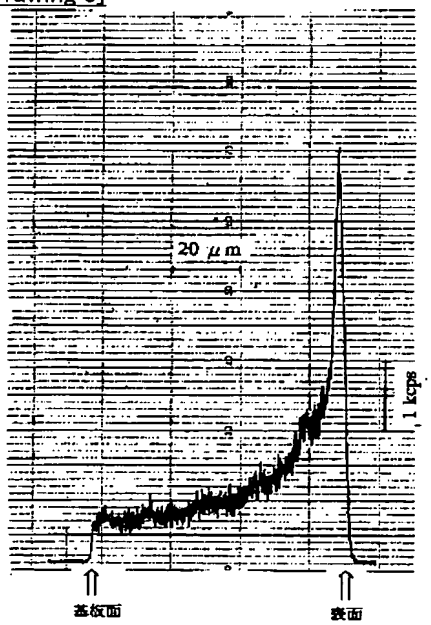
[Drawing 3]



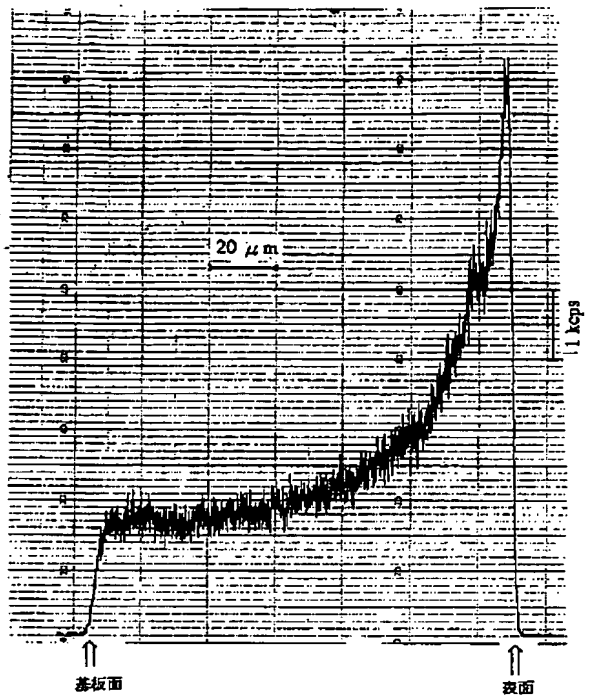
[Drawing 4]



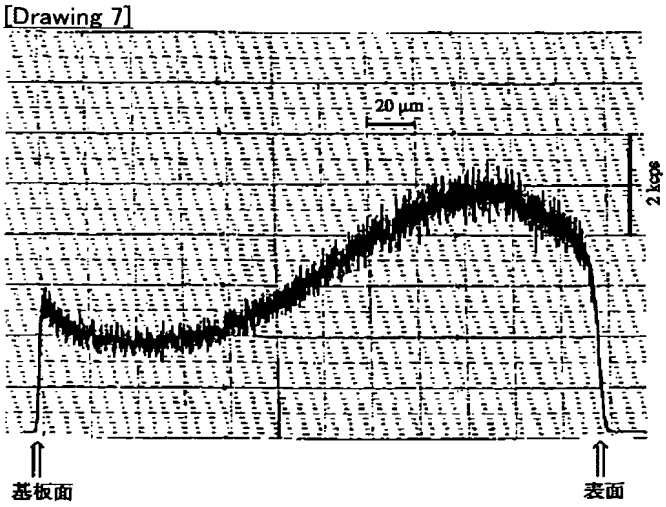
[Drawing 5]



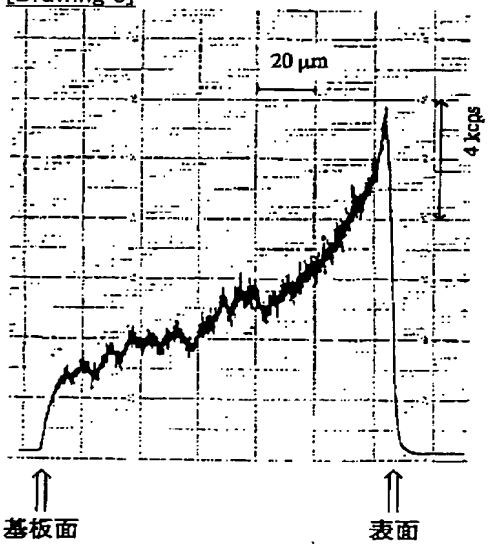
[Drawing 6]



[Drawing 7]



[Drawing 8]



[Translation done.]

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[Translation done.]

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[Application number] Japanese Patent Application No. 8-16523
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C08K 3/22 KAE
5/54 KCD
C08L 101/00 LTB

[FI]

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C08K 3/22 KAE
5/54 KCD
C08L 101/00 LTB

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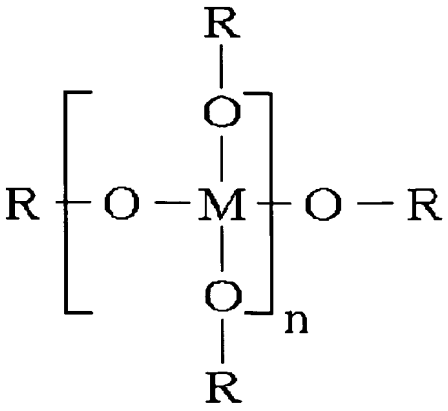
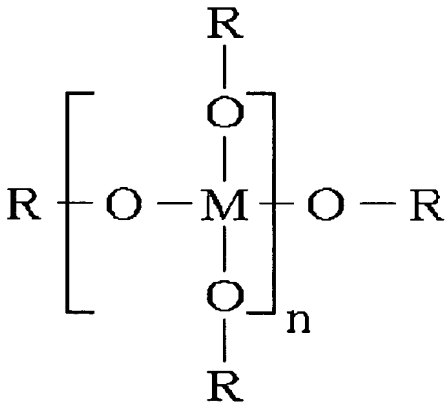
[Procedure amendment 1]
[Document to be Amended] Specification
[Item(s) to be Amended] Claim
[Method of Amendment] Modification
[Proposed Amendment]
[Claim(s)]
[Claim 1] It is the complex of the organic macromolecule and metallic oxide which are characterized by providing the following. It has the component inclination structure where the content in the inside of the complex of a metallic-oxide component (A) changes in the depth direction from the front face of complex continuously. And component inclination complex of the organic macromolecule and metallic oxide which are characterized by being 0 - 50 % of the weight, and the ratio of the content of a high place and a low place being 1.5 or more in 5 - 100 % of the weight, and the lowest location in the location where the content concerned is the highest Organic macromolecule component At least two sorts of components of a metallic-oxide component (A)
[Claim 2] Component inclination complex of the organic macromolecule and metallic oxide according to claim 1 from which a metallic-oxide component (A) is obtained under existence of an organic macromolecule component according to a metal alkoxide, or its hydrolysis and polycondensation of a low condensate.
[Claim 3] Component inclination complex of the organic macromolecule and metallic oxide according to claim 1 or 2 with which the metallic-oxide component (A) exists in at least one front face of complex exceeding the average content in the whole complex.
[Claim 4] Component inclination complex of the organic macromolecule and metallic oxide according to claim 1 or 2 with which the metallic-oxide component (A) exists by the ratio below the average content in the whole complex in at least one front face of complex.
[Claim 5] Component inclination complex of the organic macromolecule of any one publication of claim 1-4 with the larger thickness (d1) from which the content of a metallic-oxide component (A) is changing continuously in the depth direction of complex than the thickness (d2) which shows the highest content of a metallic-oxide component (A), and a metallic oxide.
[Claim 6] Component inclination complex of the organic macromolecule of any one publication of claim 1-5 and metallic oxide whose magnitude of the metallic oxide in complex is the pitch diameter of 0.01-5 micrometers.
[Claim 7] Component inclination complex of the organic macromolecule of any one publication of claim 2-6 and

metallic oxide a metal alkoxide or its low condensate of whose is what is expressed with a general formula 1.
[Formula 1]

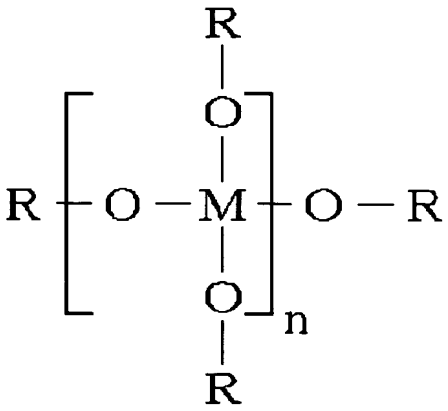


(Among a formula, in M, CmH2m+1 and m express the integer of 1-4, and, as for n, a silicon atom and R express the integer of 1-10.)
[Claim 8] The manufacture approach of the component inclination complex of the organic macromolecule and metallic oxide which are characterized by performing desiccation and heat treatment after holding what applied the homogeneity solution which consists of an organic macromolecule, metal alkoxides, and those common solvents on the organic macromolecule or the inorganic base material under the ambient atmosphere which included the polymerization catalyst of water and/or a metal alkoxide in air.
[Claim 9] The manufacturing method of the component inclination complex of the organic macromolecule and metallic oxide according to claim 8 which include an organic solvent in the air ambient atmosphere in which the polymerization catalyst of water and/or a metal alkoxide was included further.
[Claim 10] The manufacturing method of the component inclination complex of the organic macromolecule and metallic oxide according to claim 9 which are that in which the organic solvent contained in an ambient atmosphere differs from the organic solvent used for preparation of a homogeneity solution.
[Claim 11] The manufacturing method of the component inclination complex of the organic macromolecule of any one publication of claim 8-10 which includes the polymerization catalyst of a metal alkoxide further in the homogeneity solution which consists of an organic macromolecule, metal alkoxides, and those common solvents, and a metallic oxide.
[Claim 12] The manufacture approach of the component inclination complex of the organic macromolecule of any one publication of claim 8-11 and metallic oxide whose polymerization catalyst of the metal alkoxide contained in an air ambient atmosphere or a homogeneity solution is congener or an alkali of a different kind.
[Claim 13] The manufacturing method of the component inclination complex of the organic macromolecule of any one publication of claim 8-12 and metallic oxide which are the silicon alkoxide a metal alkoxide is indicated to be by the general formula 1, or its low condensate.
[Formula 2]

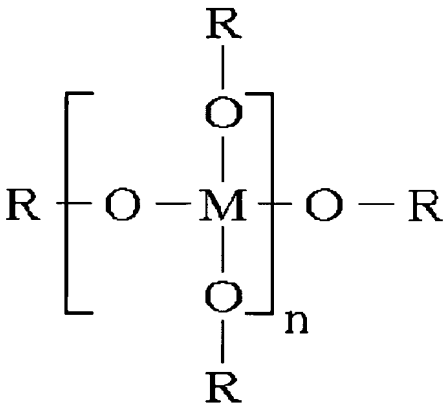


(Among a formula, in M, CmH2m+1 and m express the integer of 1-4, and, as for n, a silicon atom and R express the integer of 1-10.)
[Procedure amendment 2]
[Document to be Amended] Specification
[Item(s) to be Amended] 0020
[Method of Amendment] Modification
[Proposed Amendment]

[0020] (General formula 1)
[Formula 3]



(Among a formula, in M, CmH2m+1 and m express the integer of 1-4, and, as for n, a silicon atom and R express the integer of 1-10.)
[Procedure amendment 3]
[Document to be Amended] Specification
[Item(s) to be Amended] 0021
[Method of Amendment] Deletion
[Procedure amendment 4]
[Document to be Amended] Specification
[Item(s) to be Amended] 0022
[Method of Amendment] Deletion
[Procedure amendment 5]
[Document to be Amended] Specification
[Item(s) to be Amended] 0025
[Method of Amendment] Modification
[Proposed Amendment]
[0025] (General formula 1)
[Formula 4]



(Among a formula, in M, CmH2m+1 and m express the integer of 1-4, and, as for n, a silicon atom and R express the integer of 1-10.)

[Translation done.]

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5/54	KCD		5/54	KCD	
C08L101/00	LTB		C08L101/00	LTB	

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(54)【発明の名称】有機高分子と金属酸化物との成分傾斜複合体及びその製造法

(57)【要約】　（修正有）

【課題】　金属酸化物の高含有率領域までの特性を効果的に発現しうるような良好な複合体であり、クラックが生じ難く、かつ加熱や経時変化により表層面だけの剥離が生じるようなことが無い良好な成形性を有する、有機高分子と金属酸化物との成分傾斜複合体。

【解決手段】　有機高分子成分と、金属酸化物成分Ａの少なくとも２種の成分を含む有機高分子と金属酸化物との複合体であって、複合体の表面から深さ方向に、金属酸化物成分Ａの複合体中での含有率が連続的に変化する成分傾斜構造を有し、且つ当該含有率が最も高い場所で５～１００重量％、最も低い場所で０～５０重量％であり、且つ高い所と低い所との含有率の比が１．５以上である。有機高分子と金属アルコキシドとの均質溶液を、有機高分子または無機の基材上に塗布したものを、水及び／又は金属アルコキシドの重合触媒を空気中に含ませた雰囲気下に保持した後、乾燥、熱処理を行う。

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【特許請求の範囲】

【請求項１】　有機高分子成分と、金属酸化物成分（Ａ）の少なくとも２種の成分を含む有機高分子と金属酸化物との複合体であって、複合体の表面から深さ方向に、金属酸化物成分（Ａ）の複合体中での含有率が連続的に変化する成分傾斜構造を有し、且つ当該含有率が最も高い場所で５～１００重量％、最も低い場所で０～５０重量％であり、且つ高い所と低い所との含有率の比が１．５以上であることを特徴とする有機高分子と金属酸化物との成分傾斜複合体。

【請求項２】　金属酸化物成分（Ａ）が、有機高分子成分の存在下で金属アルコキシドまたはその低縮合物の加水分解・重縮合により得られたものであることを特徴とする請求項１記載の有機高分子と金属酸化物との成分傾斜複合体。

【請求項３】　金属酸化物成分（Ａ）が、複合体の少なくとも１つの表面において、複合体全体での平均含有率を越えて存在していることを特徴とする請求項１および２記載の有機高分子と金属酸化物との成分傾斜複合体。

【請求項４】　金属酸化物成分（Ａ）が、複合体の少なくとも１つの表面において、複合体全体での平均含有率以下の比率で存在していることを特徴とする請求項１および２記載の有機高分子と金属酸化物との成分傾斜複合体。

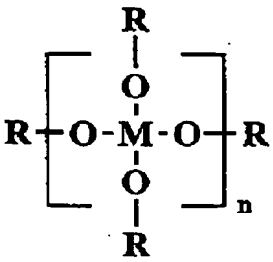
【請求項５】　複合体の深さ方向において、金属酸化物成分（Ａ）の含有率が連続的に変化している厚み（ｄ１）が、金属酸化物成分（Ａ）の最も高い含有率を示す厚み（ｄ２）より大きいことを特徴とする請求項１～４記載の有機高分子と金属酸化物との成分傾斜複合体。

【請求項６】　複合体中の金属酸化物の大きさが、平均径０．０１～５μｍであることを特徴とする請求項１～５のいずれか一つに記載の有機高分子と金属酸化物との成分傾斜複合体。

【請求項７】　複合体中の金属酸化物の大きさが、平均径０．０１～０．５μｍであることを特徴とする請求項６記載の有機高分子と金属酸化物との成分傾斜複合体。

【請求項８】　金属アルコキシドまたはその縮合物が一般式１で表されるものであることを特徴とする特許請求項２～７のいずれか一つに記載の有機高分子と金属酸化物との成分傾斜複合体。

【化１】



（式中、Ｍは珪素原子、ＲはＣｎＨ２ｎ＋１、ｍは１～４の整数、ｎは１～１０の整数を表わす。）

2

【請求項９】　有機高分子成分が熱硬化性樹脂であることを特徴とする請求項１～８のいずれか一つに記載の有機高分子と金属酸化物との成分傾斜複合体。

【請求項１０】　有機高分子成分が熱可塑性樹脂であることを特徴とする特許請求項１～８のいずれか一つに記載の有機高分子と金属酸化物との成分傾斜複合体。

【請求項１１】　有機高分子と金属アルコキシドとそれらの共通溶媒からなる均質溶液を、有機高分子または無機の基材上に塗布したものを、水及び／又は金属アルコキシドの重合触媒を空気中に含ませた雰囲気下に保持した後、乾燥、熱処理を行うことを特徴とする有機高分子と金属酸化物との成分傾斜複合体の製造方法。

【請求項１２】　水及び／又は金属アルコキシドの重合触媒を含ませた空気雰囲気に、更に有機溶媒を含ませることを特徴とする請求項１１記載の有機高分子と金属酸化物との成分成分傾斜複合体の製造法。

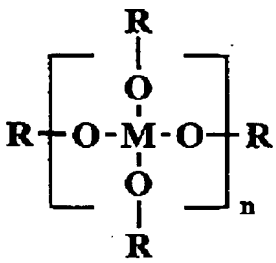
【請求項１３】　雰囲気中に含まれる有機溶媒が、均質溶液の調製に用いられる有機溶媒と異なるものであることを特徴とする請求項１２記載の有機高分子と金属酸化物との成分成分傾斜複合体の製造法。

【請求項１４】　有機高分子と金属アルコキシドとそれらの共通溶媒からなる均質溶液中に、更に金属アルコキシドの重合触媒を含ませることを特徴とする請求項１１～１３のいずれか一つに記載の有機高分子と金属酸化物との成分成分傾斜複合体の製造法。

【請求項１５】　空気雰囲気中または均質溶液中に含まれる金属アルコキシドの重合触媒が、同種または異種の塩基性物質であることを特徴とする請求項１１～１４のいずれか一つに記載の有機高分子と金属酸化物との成分傾斜複合体の製造方法。

【請求項１６】　金属アルコキシドが一般式１で示されるシリコンアルコキシドまたはその低縮合物であることを特徴とする請求項１１～１５のいずれか一つに記載の有機高分子と金属酸化物との成分成分傾斜複合体の製造法。

【化２】



（式中、Ｍは珪素原子、ＲはＣｎＨ２ｎ＋１、ｍは１～４の整数、ｎは１～１０の整数を表わす。）

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、金属アルコキシド

の加水分解・重縮合反応により得られる金属酸化物と有機高分子との複合体において、金属酸化物の含有率が複合体の厚み方向に傾斜的に異なる領域を有することを特徴とする有機高分子と金属酸化物との成分傾斜複合体とその製造法に関する。

【０００２】

【従来の技術】有機高分子の性能を改質するために、これまで種々の方法が検討されており、複数の有機高分子をブレンドして新規な特性を持つ樹脂を調製したり、異種の補強材と複合化して目的とする特性を有する成形体を調製すること等が広く行われている。

【０００３】例えば、有機高分子同士のブレンド複合化では、相溶性を示す有機高分子を探索して溶融混合等の方法で均質な複合体としたり、また非相溶性である有機高分子をミクロ相分離構造を含む特定の分散構造を持つように、混合条件を工夫してブレンドすること等で、使用目的に応じた有機高分子の改質がなされてきた。

【０００４】一方、強化材を有機高分子に混合・分散させることによる物性改質も広範囲に検討されている。具体的にはアラミド繊維、パルプ、ガラス繊維、炭素繊維等の有機または無機の繊維状物質や炭酸カルシウム、シリカ、アルミナ等の粉末状無機材料等を有機高分子と混合することが広く行われている。

【０００５】特に無機材料との混合による複合化は、無機材料の優れた耐熱性や機械的性質を生かせることから、容易な高性能改質手段として広く検討されてきている。しかし無機材料の場合、その熱不溶融性、薬品不溶解性、高比重、表面特性などの点での有機高分子材料との本質的な性質の違いから、分散状態をミクロに制御することは簡単ではなく、もっぱら出来るだけ均質なバルク複合材料を得ることを目的として複合化されるのが一般的である。

【０００６】即ち、改質効果を上げる為に、より小さい形状を持ち、且つマトリックス高分子との濡れ性の良いものを補強用無機材料として選択し、それらを所定量だけ、出来るだけ均質に分散することが複合化における重要な因子となっている。しかしこの場合でも、無機材料は微粒子状になる程、均質分散が困難となり、またエネルギー、コスト的にも高いものとなる問題がある。

【０００７】従って、有機材料と微粒子状無機材料とから成る、ミクロ的に均質で、且つ分散構造が制御された、高性能の有機材料と無機材料との複合材を得るためには、上述のような単に微粒子状の無機材料を有機高分子と混合する方法では全く困難であり、新しい技術の開発が必要である。

【０００８】本発明者らは、このような目的に対して有効な新規の有機材と無機材との複合材の開発研究を行ってきた。その一例として、例えば、金属アルコキシドから得られる金属酸化物と有機高分子とのミクロハイブリッド複合材料がある。

【０００９】該複合体は有機高分子マトリックス中にて、ｉｎ－ｓｉｔｕで金属アルコキシドの加水分解・重縮合を行うことにより、ナノオーダーからミクロンオーダーの金属酸化物粒子が有機高分子中に濡れ性良く、均質に分散・複合化されたものであり、機械的性質を始めとして非常に優れた特性を有する有機材と無機材との複合材料である。

【００１０】しかしながら、該複合体中の金属酸化物成分割合を過度に大きくしていくと、複合化する有機高分子と金属酸化物との本質的な特性の差により良好な複合材が得られなくなってくる。即ち、金属酸化物含有率が高いものではクラックが生じ易くなったり、脆くなったり、成形性が悪くなったり、また反り、歪等の変形を生じたりする。一方、金属酸化物含有率が微量のものでは、所望の複合物性が得られなくなる。

【００１１】

【発明が解決しようとする課題】本発明が解決しようとする課題は、金属酸化物の高含有率領域までの特性を効果的に発現しうるような良好な複合体を得ることであり、より具体的にはクラックが生じ難く、かつ加熱や経時変化により表層面だけの剥離が生じるようなことが無い良好な成形性を有する、有機高分子と金属酸化物との成分傾斜複合体及びその製造法を提供することにある。

【００１２】

【課題を解決するための手段】本発明者等は有機高分子と金属酸化物からなる複合体において、広範囲な組成領域の優れた特性を有する複合体を得るべく鋭意研究に取り組み、本研究を完成するに至ったものである。

【００１３】即ち、本発明は有機高分子成分と、金属酸化物成分（Ａ）の少なくとも２種の成分を含む有機高分子と金属酸化物との複合体であって、複合体の表面から深さ方向に、金属酸化物成分（Ａ）の複合体中での含有率が連続的に変化する、成分傾斜構造を有し、且つ当該含有率が最も高い場所で５～１００重量％、最も低い場所で０～５０重量％であり、且つ高い所と低い所との含有率の比が１．５以上であることを特徴とする有機高分子と金属酸化物との成分傾斜複合体である。

【００１４】本発明の有機高分子と金属酸化物との成分傾斜複合体は、詳しくは、その金属酸化物成分（Ａ）が、有機高分子成分の存在下で金属アルコキシドまたはその低縮合物の加水分解・重縮合により得られたものであることを特徴とする有機高分子と金属酸化物との成分傾斜複合体である。

【００１５】また本発明の有機高分子と金属酸化物との成分傾斜複合体は、詳しくは、金属酸化物成分（Ａ）が、複合体の少なくとも１つの表面において、複合体全体での平均含有率を越えて存在していることを特徴とするものである。

【００１６】更に本発明の有機高分子と金属酸化物との成分傾斜複合体は、金属酸化物成分（Ａ）が、複合体の

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少なくとも１つの表面において、複合体全体での平均含有率以下の比率で存在していることを特徴とする有機高分子と金属酸化物との成分傾斜複合体である。

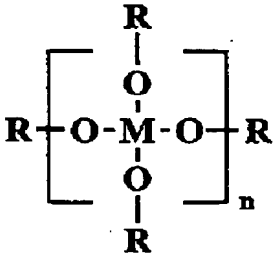
【００１７】また本発明の有機高分子と金属酸化物との成分傾斜複合体は、複合体の深さ方向において、金属酸化物成分（Ａ）の含有率が連続的に変化している厚み（ｄ１）が、金属酸化物成分（Ａ）の最も高い含有率を示す厚み（ｄ２）より大きいことを特徴とする有機高分子と金属酸化物との成分傾斜複合体である。

【００１８】更に、本発明の有機高分子と金属酸化物との成分傾斜複合体は、複合体中の金属酸化物の大きさが、平均径０．０１～５μｍであることを特徴とする有機高分子と金属酸化物との成分傾斜複合体と、複合体中の金属酸化物の大きさが、平均径０．０１～０．５μｍであることを特徴とする有機高分子と金属酸化物との成分傾斜複合体を含むものである。

【００１９】また本発明の有機高分子と金属酸化物との成分傾斜複合体は、その金属酸化物成分が、有機高分子成分の存在下で金属アルコキシドまたはその低縮合物の加水分解・重縮合により得られたものであり、特にその金属アルコキシドまたはその縮合物が一般式１で表されるものであることを特徴とする有機高分子と金属酸化物との成分傾斜複合体である。

【００２０】（一般式１）

【化３】



（式中、Ｍは珪素原子、ＲはＣ$_m$Ｈ$_{2m+1}$、ｍは１～４の整数、ｎは１～１０の整数を表わす。）

【００２１】また本発明の有機高分子と金属酸化物との成分傾斜複合体は、有機高分子成分が熱硬化性樹脂であることを特徴とする有機高分子と金属酸化物との成分傾斜複合体である。

【００２２】また本発明の有機高分子と金属酸化物との成分傾斜複合体は、有機高分子成分が熱可塑性樹脂であることを特徴とする有機高分子と金属酸化物との成分傾斜複合体である。

【００２３】本発明は、有機高分子と金属アルコキシドとそれらの共通溶媒及び／又は金属アルコキシドの重合触媒からなる均質溶液を、有機高分子または無機の基材上に塗布したものを、水及び／又は金属アルコキシドの重合触媒及び／又は有機溶媒を空気中に含ませた雰囲気下に保持した後、乾燥、熱処理を行うことを特徴とする有機高分子と金属酸化物との成分傾斜複合体の製造方法

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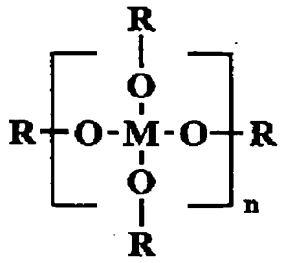
を含むものである。

【００２４】本発明の有機高分子と金属酸化物との成分傾斜複合体の製造方法は、その金属酸化物成分が、有機高分子成分の存在下で金属アルコキシドまたはその低縮合物の加水分解・重縮合により、有機高分子成分中に均質に分散して得られたものであり、特に金属アルコキシドが一般式１で示されるシリコンアルコキシドまたはその低縮合物であることを特徴とする有機高分子と金属酸化物との成分成分傾斜複合体の製造法である。

【００２５】（一般式１）

【化４】



（式中、Ｍは珪素原子、ＲはＣ$_m$Ｈ$_{2m+1}$、ｍは１～４の整数、ｎは１～１０の整数を表わす。）

【００２６】また本発明の有機高分子と金属酸化物との成分傾斜複合体の製造方法は、特に雰囲気中及び／又は均質溶液中に含まれる金属アルコキシドの重合触媒として、同種または異種の塩基性物質を用いることを特徴とする有機高分子と金属酸化物との成分傾斜複合体の製造方法を含むものである。

【００２７】即ち、本発明は、少なくとも１種ずつの有機高分子と金属酸化物を含有する有機高分子と金属酸化物との複合体において、含有される金属酸化物成分が複合体の内部において異なる濃度で存在し、複合体の表面から深さ方向に、金属酸化物成分濃度が連続的に変化する成分傾斜構造を形成していること、

【００２８】且つ複合体中の金属酸化物成分濃度が最も高い所で５～１００重量％、最も低いところで０～５０重量％であること、且つ高い所と低い所との含有率の比が１．５以上であることを特徴とする有機高分子と金属酸化物との成分傾斜複合体に関するものであり、特に有機高分子存在下で金属アルコキシドまたはその低縮合物を重縮合して得られる金属酸化物と有機高分子からなる、有機高分子と金属酸化物との成分傾斜複合体を中心としたものである。

【００２９】当該有機高分子と金属酸化物との成分傾斜複合体では、複合体の少なくとも１つの表面において、金属酸化物成分が複合体の平均金属酸化物濃度を越えて存在しているもの、または少なくとも１つの表面において金属酸化物成分が複合体の平均金属酸化物濃度以下であるものを含む。また当該有機高分子と金属酸化物との成分傾斜複合体は、深さ方向において金属酸化物の最高含有率を有する厚みより金属酸化物濃度傾斜を有する厚

みが大きいものを含むものである。

【００３０】また当該有機高分子と金属酸化物との成分傾斜複合体は、複合体中に含有される金属酸化物の大きさが平均径０．０１μｍ～５μｍであるものを含む。また当該有機高分子と金属酸化物との成分傾斜複合体は、その形態が塗膜や糸、フィルム、球状のものであるほかブロック等の各種形状の成形体であるものを含む。

【００３１】本発明においては、金属酸化物が有機高分子中において深さ方向以外では均質性を保ちながら、深さ方向に連続的に変化している領域を有することを基本とする。従って、単に不規則な凝集や相分離により、不連続的に金属酸化物濃度の異なる領域を有するものや、塗装により形成される一定金属酸化物含有率を有する均一塗膜を基材の表面上に有するものなどとは異なる。

【００３２】本発明に使用できる有機高分子としては、有機高分子存在下での金属アルコキシドの重縮合により、均質な有機高分子と金属酸化物との複合体をつくることが可能なものであればよく、特に限定されないが、具体的には、例えばフェノール樹脂、エポキシ樹脂、アクリル樹脂、アルキド樹脂、メラミン樹脂、尿素樹脂等の熱硬化性樹脂やナイロン、ポリエステル、アクリル樹脂等の熱可塑性樹脂、またポリブタジエンやＳＢＳのようなゴム系樹脂等を用いることが可能であり、特に熱硬化性樹脂、中でもエポキシ樹脂、アクリル樹脂、アルキド樹脂、メラミン樹脂が好ましい。

【００３３】製造上の容易さからの観点では、金属アルコキシドやその縮合物またはそれらと溶媒等からなる均質溶液に溶解するか、または膨潤する有機高分子またはその前駆体樹脂であるものが望ましい。

【００３４】本発明における金属アルコキシドとしては、一般式１に示されるシリコンアルコキシド及び／またはその縮合物が用いられる。その他の金属アルコキシド類としては、Ｔｉ、Ａｌ、Ｚｒ等の金属アルコキシドも可能であるが、Ｓｉのアルコキシド類、またはＳｉを主成分とする他金属アルコキシド類との混合物を用いると、加水分解・重縮合の反応速度が緩やかで濃度傾斜を制御する上で特に好ましい。

【００３５】本発明における有機高分子と金属酸化物との成分傾斜複合体は、金属酸化物成分（Ａ）の複合体中での含有率（以下、単に金属酸化物含有率と言うことがある。）の最も高い部分が５～１００重量％であり、最も低い部分では０～５０重量％であるものが好ましい。

【００３６】最も高い部分での金属酸化物含有率が５重量％未満では、複合化の効果が不十分であり、また最も低い部分での金属酸化物含有率が５０重量％を越えるものは複合体が脆くなったり、クラック等の発生が生じ易くなったり、また複合体全体の厚みが非常に薄くなくてはならない等の制限が大きくなり、好ましくない。

【００３７】また金属酸化物含有率の最も高い所と低い所との比は１．５以上、好ましくは２以上であることが必要である。当該比が１．５未満では成分傾斜複合体としての効果が不十分である。また金属酸化物濃度が深さ方向に傾斜的に変化している厚み（ｄ１）が、最も高い金属酸化物含有率を示す領域の厚み（ｄ２）より大きい場合に傾斜複合材としての効果がより明確である。

【００３８】本発明における金属酸化物の大きさとしては、直径０．０１μｍ～５μｍである。特に金属酸化物の大きさが０．０１μｍ～０．５μｍで、用いる有機高分子が透明なものである場合は、本発明の複合体は透明～半透明の外観を有する。また金属酸化物の大きさが０．５μｍ～５μｍの場合は、半透明～不透明の外観を有する。

【００３９】いずれにしても、金属アルコキシドまたはその縮合物を有機高分子存在下で重縮合させて得られる金属酸化物と有機高分子からなる成分傾斜複合体では、予め製造された金属酸化物粒子と有機高分子を混合分散させるのに比べて、金属酸化物粒子の粒径制御が極微小粒径まで容易である。

【００４０】従来のシリカ等の補強添加用粒子としては、直径１～２μｍ程度のものまでが均質分散の可能性またコスト的にみて、その限界となっている。さらに小さい微粒子を用いる場合は、有機高分子との密度差や微粒子の凝集により、均質な分散またはその制御が困難である場合が多い。

【００４１】本発明においては、金属酸化物の平均粒径がナノメーターサイズのものまで均質に含まれ、且つ分散構造制御された成分傾斜複合体を得ることができる。本発明における金属酸化物の大きさは、走差型電子顕微鏡等による測定では０．０１μｍ以下の粒径をとらえるのが難しいことから０．０１μｍの数値を付しているが、０．０１μｍより小さくてもなんら差し支えない。しかし平均粒径が５μｍ以上では均質な成分傾斜複合体が得られ難くなる。

【００４２】本発明の有機高分子と金属酸化物との成分傾斜複合体を得る方法としては、最終的に得られる成分傾斜複合体がミクロ的に均質な分散を保ちながら、且つ複合体の深さ方向に連続的に金属酸化物濃度が変化する領域を有するものであれば良く、特に製造方法によって限定されないものである。

【００４３】しかしながら、その具体的製造方法の一例を挙げれば、例えば、有機高分子成分及び金属アルコキシドまたはその縮合物、及び／又は水、及び／または触媒、及び／または有機溶媒を原料として用いて、金属アルコキシドの加水分解・重縮合、樹脂の硬化反応、及び／または溶媒キャストを行わせる際に、最終的に得られる複合体の深さ方向において不均一な金属アルコキシド類の加水分解・重縮合を生じるような操作を行うものである。

【００４４】更に具体的には、上記原料の内、特定の原料成分（例えば、金属アルコキシドや塩基性触媒や水）

の濃度分布を深さ方向にもたせたり、一方向からの外部刺激（例えば加熱）を行うことにより、傾斜的な金属酸化物濃度分布を発現させることが可能である。

【００４５】例えば、有機高分子と金属アルコキシドまたはその縮合物とそれらの共通溶媒及び／又は金属アルコキシドの重合触媒からなる均質溶液を基材上に塗布したものを、水及び／又は金属アルコキシドの重合触媒及び／又は有機溶媒を空気中に含ませてなる雰囲気下に保持した後、乾燥、熱処理を行うことで、塗膜中での金属酸化物濃度の傾斜を発現させることができる。

【００４６】本発明において、雰囲気中または均質溶液中に含まれる金属アルコキシドの重合触媒としては同一または異種の酸または塩基性物質が用いられるが、特に各種アミン化合物やアンモニアのような塩基性物質を用いるのは傾斜複合体中の金属酸化物の微粒子化や成分傾斜制御において好ましい。

【００４７】また本発明において雰囲気中に含まれる有機溶媒としては、有機高分子等からなる溶液と均質に混和するものが好ましく、また溶液中に既に含まれている有機溶媒とは異なる種類のものであるのが特に好ましい。

【００４８】本発明の有機高分子と金属酸化物との成分傾斜複合体は、塗膜や糸、フィルム、微粒子等の各種成形体や成形原料に用いることが可能である。また他の金属やガラス等の無機繊維及び／またはセルロースやアラミド等有機繊維及び／またはそれらの粉末を含んだ系にて調製することも可能である。

【００４９】本発明の有機高分子と金属酸化物との成分傾斜複合体では、例えば複合体全体の金属酸化物の平均濃度が非常に低いにもかかわらず、少なくとも１つの表面部に５～１００重量％と高い金属酸化物濃度を有しており、且つその表面部から内部にかけて傾斜的にその濃度が漸減している分散状態の構造を有するものが可能である。

【００５０】従って、この場合は表面部のみは金属酸化物濃度がより高いことによる特性、例えば、高硬度や優れた耐溶剤性、耐熱性を有するが、その層は表面からの一定厚みに限定されるため、例えばクラック等による劣化因子が見られず、且つ内部にかけて成分傾斜的になっているために、加熱や経時変化により表層面だけの剥離が生じるようなことが無く、安定した複合材特性を発現することができる。逆に、内部の金属酸化物濃度が表面部より高いものや、より複雑に多層濃度分布を示すものも可能である。

【００５１】

【実施例】次いで本発明を実施例によって更に説明する。尚、例中の％は特に断りの無い限り重量基準である。

【００５２】（実施例１）アクリル樹脂（大日本インキ化学工業株式会社製：アクリディック　Ａ－４０５）３０ｇ（樹脂分５７％；キシレン、ブタノール溶液）、メラミン樹脂（大日本インキ化学工業株式会社製：スーパーベッカミン　Ｇ－８２１）６.５ｇ（樹脂分６０％；イソブチル溶液）、エポキシ樹脂（大日本インキ化学工業株式会社製：エピクロン　１０５０）２.５ｇ、テトラメトキシシラン（以下、ＴＭＯＳと呼ぶ。：東京化成工業社製　特級試薬）１０ｇ、及び脱水テトラヒドロフラン（ＴＨＦ；関東化学株式会社製　特級試薬）２０ｇからなる均質溶液を

【００５３】基材（ナイロン－６６板）上に滴下し、０.０９モル／ｌのアンモニア濃度の飽和水蒸気雰囲気下で約５時間放置した後、更に、２８℃、５０％に約１日間放置した。８０℃で２時間、更に１５０℃で１時間熱処理を行いアクリル樹脂／シリカ系からなる塗膜（約４０ミクロン厚）を得た。

【００５４】電子線マイクロアナライザー（ＥＰＭＡ）を用いて、塗膜の断面のＳｉの分布を表面からスキャンした結果を図１に示す。図１の結果より、表面側に強いＳｉの分布が見られ、且つ約４０ミクロンの深さ方向に渡って連続的にＳｉ濃度が変化していることが認められる。

【００５５】また、かかる深さ方向のＳｉ濃度分布は、同じ塗膜の異なる数カ所の位置で測定しても同じ分布を示すことより、深さ方向と直角の方向には均質なＳｉ濃度を保持していることがわかった。以上の結果より、得られた塗膜は、塗膜全体の平均金属酸化物濃度より高い濃度のシリカ含有層を表面部に持ち、深さ方向と直角方向には均質で、且つ深さ方向には連続的な濃度変化を有する複合体（塗膜）であることが確認された。ここで、

【００５６】濃度傾斜領域の厚み＝約２３μｍ、濃度傾斜領域厚み／全体厚み＝０．５４

濃度傾斜領域厚み／最大濃度領域厚み＝約９

最大金属酸化物濃度／最低金属酸化物濃度＝２８重量％／３.５重量％＝７.３であった。

【００５７】この成分傾斜複合体は薄い白濁を呈しており、走査型電子顕微鏡（ＳＥＭ）を用いて塗膜断面の観測を行ったところ、直径０．２～０．４μｍの大きさのシリカ微粒子が観測された。シリカ粒子の分布の状態は均質であるが、塗膜表面付近で高く分布し、塗膜内部に行くにつれて低下していた。

【００５８】尚、ＥＰＭＡは島津製作所株式会社製のＥＰＭ－８１０型を用いて、出力１５ｋＶ－５０ｎＡ、分解能１～１.５ミクロン、１０ミクロン／分のスキャン速度、検出はＳｉのＫα線（７.１２６オングストローム）で行った。また、ＳＥＭは、日立製作所株式会社製のＳ－８００型のオームストロングＳＥＭを用い、約３ｎｍのプラチナをスパッタリングした試料で観測を行った。

【００５９】（実施例２）実施例１の製造条件において、ＴＨＦ２０ｇのかわりにメタノール２０ｇを用い、

更に均質溶液のキャストをアンモニア水の飽和水蒸気中で行う代わりに、２５℃、５０％の雰囲気下で行った場合について検討した。透明性に優れた塗膜が得られた。ＥＰＭＡ測定の結果を図２に示す。基盤側に高い金属酸化物濃度を有する成分傾斜複合体となっているのがわかる。

【００６０】濃度傾斜領域の厚み＝４０μｍ、濃度傾斜領域厚み／全体厚み＝０．７

濃度傾斜領域厚み／最大濃度領域厚み＝１０

最大金属酸化物濃度／最低金属酸化物濃度＝１１．５重量％／４．５重量％＝２．５であった。

【００６１】成分傾斜複合体は透明で、ＳＥＭ観測では直径約０．０４～０．１μｍの微粒子がミクロな範囲で均質に分散しているのが観測された。

【００６２】（比較例１）実施例１の均質溶液に５ｇの蒸留水を添加して得られる均質溶液を用いて、実施例１と同様な手法でサンプルを作成し検討を行った。ＥＰＭＡ測定の結果を図３に示す。シリカ濃度に傾斜は見られなく、均質に分布しているのが判る。

【００６３】濃度傾斜領域の厚み＝０μｍ、

最大金属酸化物濃度／最低金属酸化物濃度＝１２重量％／１１重量％＝１．１

複合体は透明で、ＳＥＭ観測では直径０．０６～０．１５μｍの微粒子が均質に分散しているのが確認された。

【００６４】（比較例２）実施例１におけるアンモニア水のアンモニア濃度を０．５モル／ｌとした場合について、実施例１と同様な方法でサンプルを調製し検討を行った。ＥＰＭＡ測定の結果を図４に示す。シリカ濃度に傾斜は見られなく、均質に分布しているのが判る。

【００６５】濃度傾斜領域の厚み＝０μｍ、

最大金属酸化物濃度／最低金属酸化物濃度＝１３．５重量％／１２．５重量％＝１．１で複合体は透明体であった。

【００６６】（実施例３）実施例１と同じ均質溶液をナイロン－６６板上に滴下し、０．０６モル／ｌのアンモニア水とメタノールの１０：３（重量比）混合溶液の飽和水蒸気雰囲気下で２２℃で約１０時間放置した後、実施例１と同様な処理を行いアクリル樹脂／シリカ系からなる塗膜（約７５ミクロン厚）を得た。ＥＰＭＡ測定の結果を図５に示す。塗膜表面側に極めて高いシリカ濃度を有する傾斜複合体が得られているのが判る。

【００６７】濃度傾斜領域厚み＝４０μｍ、濃度傾斜領域厚み／全体厚み＝０．５３

濃度傾斜領域厚み／最大濃度領域厚み＝１３．３

最大金属酸化物濃度／最低金属酸化物濃度＝３０重量％／３重量％＝１０

傾斜複合体は白濁を呈しており、ＳＥＭ観測では直径約０．３～２μｍの粒子がミクロな範囲で均質に分散しているのが観測された。

【００６８】（実施例４）実施例１と同じ均質溶液に更

に０．０６ｇのトリエチルアミン（東京化成工業株式会社製、特級試薬）を添加して得られる均質溶液を用いて、実施例３と同様な条件で溶媒キャストと熱処理を行いアクリル樹脂／シリカ系からなる塗膜（約１２０ミクロン厚）を得た。ＥＰＭＡ測定の結果を図６に示す。塗膜表面側に高いシリカ濃度を有する傾斜複合体となっているのが判る。

【００６９】濃度傾斜領域厚み＝７０μｍ、濃度傾斜領域厚み／全体厚み＝０．５８

濃度傾斜領域厚み／最大濃度領域厚み＝１７．５

最大金属酸化物濃度／最低金属酸化物濃度＝４０重量％／７．５重量％＝５．３

【００７０】実施例３の複合体に比べて、金属酸化物の濃度傾斜がなだらかになっている。傾斜複合体は薄い白濁を呈しており、ＳＥＭ観測では直径約６０～２００ｎｍの微粒子がミクロな範囲で均質に分散しているのが観測された。実施例３の複合体に比べて、粒径の小さな分散粒子が得られた。

【００７１】（実施例５）ビスフェノール型エポキシ樹脂（大日本インキ化学工業株式会社製：エピクロン　８５０）１０ｇと脂肪族ポリアミン系エポキシ硬化剤（大日本インキ化学工業株式会社製：エピクロン　Ｂ－０５３）２ｇとＴＨＦ　５ｇの混合溶液を室温で２６時間混合撹拌させた後、５ｇのＴＭＯＳを均質に混合した。得られた均質ゾル溶液を基板に塗布し、室温（１８℃、４０％）で溶媒キャストし、８０℃で５時間、１５０℃で３時間熱処理を行いエポキシ樹脂とシリカとの複合体を得た。ＥＰＭＡ測定の結果を図７に示す。塗膜表面の約５０μｍ内部にシリカ濃度が最大となる形態の傾斜複合体となっているのが判る。

【００７２】濃度傾斜領域厚み＝１７０μｍ、濃度傾斜領域厚み／全体厚み＝０．７、濃度傾斜領域厚み／最大濃度領域厚み＝８．５、最大金属酸化物濃度／最低金属酸化物濃度＝２６．５重量％／１０．０重量％＝２．６５であった。傾斜複合体は均質透明であり、ＳＥＭ観測では直径約３０～２００ｎｍの微粒子がミクロな範囲で均質に分散しているのが観測された。

【００７３】（実施例６）アルキド樹脂（大日本インキ化学工業株式会社製：ベッコゾール　１３４３）１５ｇとブチル化メラミン樹脂（大日本インキ化学工業株式会社製：スーパーベッカミン　Ｇ－８２１－６０）５ｇとエタノール　１０ｇとＴＭＯＳ　５ｇの混合溶液を撹拌し、均質ゾル溶液を得た。得られた均質ゾル溶液を基板に塗布し、０．４モル／ｌのアンモニア水の雰囲気下（３０℃）で溶媒キャストをした後、８０℃で５時間、１５０℃で１時間熱処理を行いアルキド樹脂とシリカとの複合体を得た。ＥＰＭＡ測定の結果を図８に示す。塗膜表面部にシリカ濃度が最大となる形態の傾斜複合体となっているのが判る。傾斜は膜厚（約１２０μｍ）全体に渡って形成されており、乳白濁化していた。

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【００７４】濃度傾斜領域厚み＝１２０μｍ、濃度傾斜領域厚み／全体厚み＝１、濃度傾斜領域厚み／最大濃度領域厚み＝１２０以上、最大金属酸化物濃度／最低金属酸化物濃度＝６２重量％／１４重量％＝４．４であった。

【００７５】

【発明の効果】本発明により得られる有機高分子と金属酸化物との成分傾斜複合体は、有機高分子中に種々の大きさ（μｍオーダーから約１０ｎｍまで）の金属酸化物を極めて均質に分散させ、且つ当該複合体の厚み方向に金属酸化物の含有濃度が分布を持つように分散されているため、例えば、表面部もしくは内部に、複合体全体での金属酸化物の平均濃度よりも高い（低い）金属酸化物濃度を有する部分を有する複合体の製造が可能で、高（もしくは低）金属酸化物濃度を含有する有機高分子複合体特有の物性を有し、且つ金属酸化物濃度が傾斜的に変化していることにより、一般の塗膜のように加熱や経時変化により表層面と内部の剥離が生じるようなことがない、安定な複合材を提供できる。

【図面の簡単な説明】

【図１】実施例１で得られた有機高分子と金属酸化物との成分傾斜複合体（塗膜）の厚み方向の電子線マイクロアナライザー（ＥＰＭＡ）によるＳｉ分布測定結果を示す図である。

【図２】実施例２で得られた有機高分子と金属酸化物との成分傾斜複合体（塗膜）の厚み方向のＥＰＭＡによるＳｉ分布測定結果を示す図である。

【図３】比較例１で得られた有機高分子と金属酸化物との複合体（塗膜）の厚み方向のＥＰＭＡによるＳｉ分布測定結果を示す図である。

【図４】比較例２で得られた有機高分子と金属酸化物との複合体（塗膜）の厚み方向のＥＰＭＡによるＳｉ分布測定結果を示す図である。

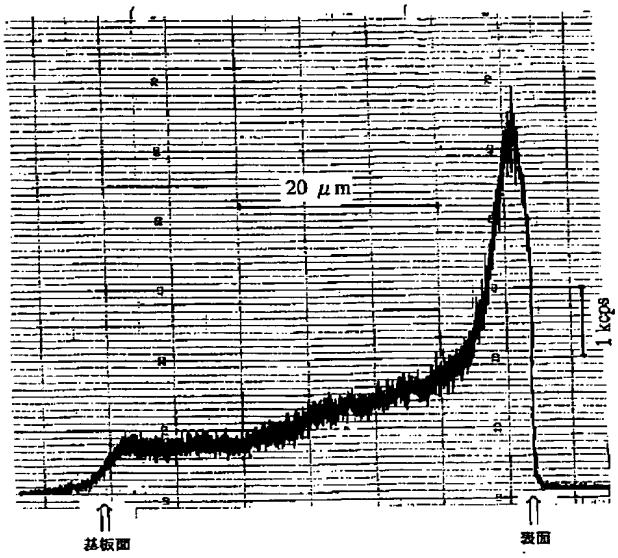
【図５】実施例３で得られた有機高分子と金属酸化物との成分傾斜複合体（塗膜）の厚み方向のＥＰＭＡによるＳｉ分布測定結果を示す図である。

【図６】実施例４で得られた有機高分子と金属酸化物との成分傾斜複合体（塗膜）の厚み方向のＥＰＭＡによるＳｉ分布測定結果を示す図である。

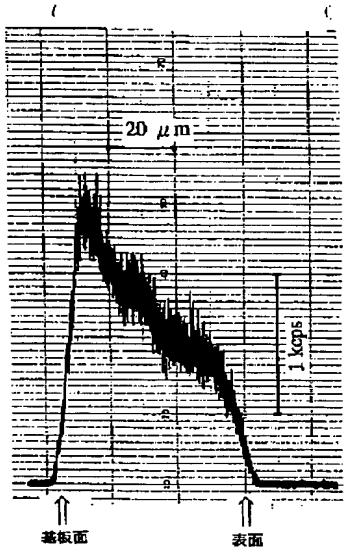
【図７】実施例５で得られた有機高分子と金属酸化物との成分傾斜複合体（塗膜）の厚み方向のＥＰＭＡによるＳｉ分布測定結果を示す図である。

【図８】実施例６で得られた有機高分子と金属酸化物との成分傾斜複合体（塗膜）の厚み方向のＥＰＭＡによるＳｉ分布測定結果を示す図である。

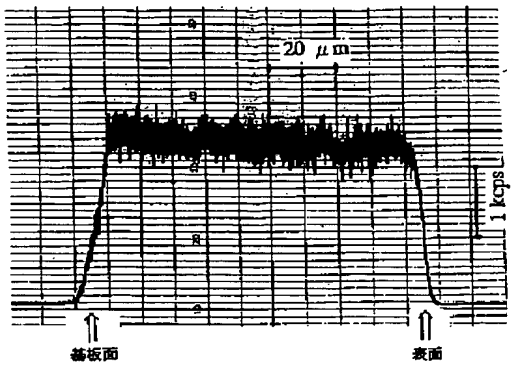
【図１】



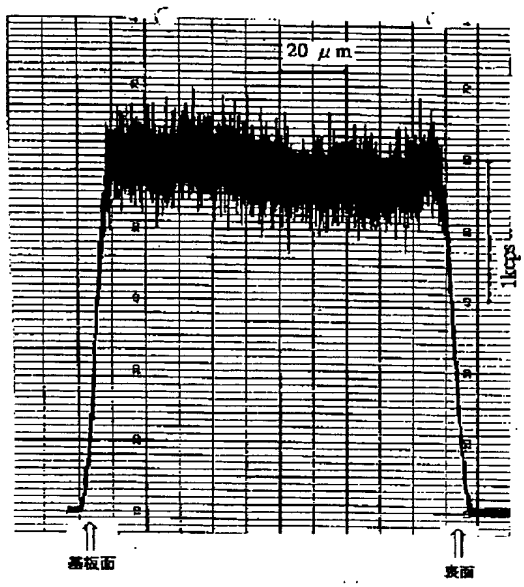
【図２】



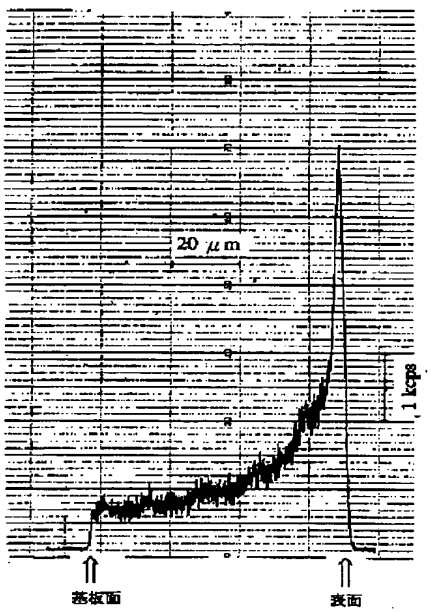
【図３】



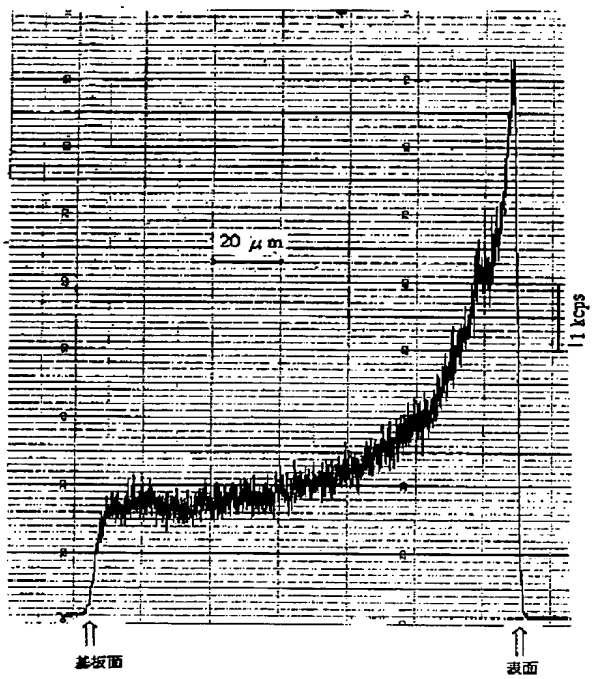
【図４】



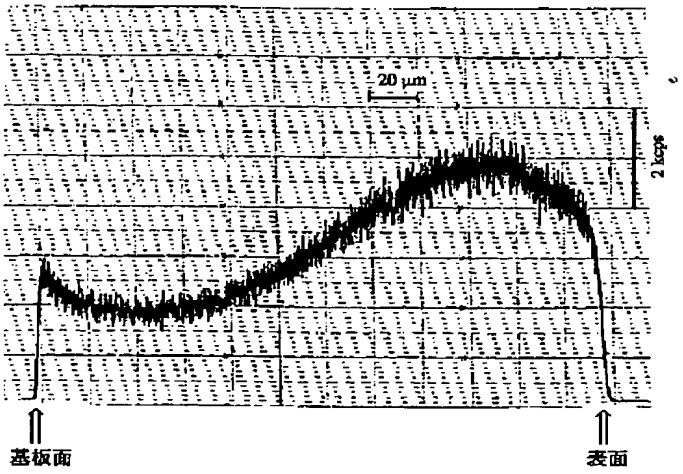
【図５】



【図６】



【図７】



【図８】